A Calorimetric Study on the Formation of $[CuCl_n]^{(2-n)+}$ (n=1—4) in Acetonitrile-*N*,*N*-Dimethylformamide Mixtures

Shin-ichi Ishiguro, Bojana G. Jeliazkova,† and Hitoshi Ohtaki*
Department of Electronic Chemistry, Tokyo Institute of Technology at Nagatsuta, 4259, Nagatsuta-cho, Midori-ku, Yokohama 227
†Department of Analytical Chemistry, Sofia University, Anton Ivanov 1, Sofia, Bulgaria

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Complex formation equilibria between copper(II) and chloride ions have been studied by calorimetry in various acetonitrile(AN)-*N*,*N*-dimethylformamide(DMF) mixtures containing 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ as a constant ionic medium at 25 °C. Calorimetric titration curves in each AN-DMF mixture examined were well explained in terms of formation of $[CuCl_n]^{(2-n)+}$ (n=1—4), and their formation constants, enthalpies, and entropies were determined. The overall enthalpy $\Delta H^\circ_{\beta 4}$ in any mixture, even in the acetonitrile-rich 0.025 mole fraction DMF mixture, was practically the same as that (19.2 kJ mol^{-1}) in pure DMF, but largely different from that (−54.5 kJ mol^{-1}) in pure AN. The result indicated that copper(II) ion was markedly preferentially solvated with DMF molecules in AN-DMF mixtures. On the other hand, the overall entropy value $\Delta S^\circ_{\beta 4}$ in any AN-DMF mixture was significantly larger than the values in both pure solvents. As to thermodynamic quantities of stepwise formation of $[CuCl_n]^{(2-n)+}$ (n=1—4), a remarkable change was found at the second step with varying solvent compositions. The stepwise enthalpy and entropy values of formation of $[CuCl_2]$ became more positive as the DMF content of the mixture decreased. Enthalpies of solution of anhydrous $CuCl_2$ crystals were also measured in the same AN-DMF mixtures. The enthalpy $\Delta H^\circ_s(CuCl_2)$ of solution of the neutral $[CuCl_2]$ complex largely changed depending on the solvent composition, while $\Delta H^\circ_s(Cu^{2+}, 2Cl^-)$, which is the sum of enthalpies of solution of relevant ions, remained practically unchanged. The result for the $[CuCl_2]$ complex indicated that the complex was not strongly preferentially solvated with DMF molecules in contrast to copper(II) ion in the AN-DMF mixtures.

In both acetonitrile (AN) and *N*,*N*-dimethylformamide (DMF), copper(II) ion forms a series of four mononuclear complexes with chloride ions, although the formation of the complex is more favorable in the former solvent than in the latter.[1—4]

The donor property of AN (the donor number (D_N)= 14.1) is much weaker than that of DMF (D_N=26.6), while the acceptor property is similar in both solvents (the acceptor number (A_N)=19.3 and 16.0 for AN and DMF, respectively).[5] Consequently, copper(II) ion is more strongly solvated with DMF than with AN. On the other hand, since the enthalpy of transfer of the chloride ion from AN to DMF is close to zero,[6] the extent of solvation of the ion may not largely differ in these solvents. Therefore, more favorable formation of the copper(II) chloro complexes in AN than in DMF is mainly ascribed to a weaker solvation of copper(II) ion in the former solvent than in the latter.

Copper(II) ion is strongly coordinated with four DMF molecules in its first coordination sphere to form the $[Cu(dmf)_4]^{2+}$ solvate even in acetonitrile-rich AN-DMF mixtures.[7]

Copper(II) ion within its chloro complexes except for $[CuCl_4]^{2-}$ may be also solvated with solvent molecules in the first solvation sphere of the metal ion in AN-DMF mixtures. The metal ion prefers DMF owing to a stronger donicity of DMF than that of AN. However, the electron acceptor ability of copper(II) ion decreases with increasing number of chloride ions within the complexes due to the electron donation from the ligands to the metal ion. Thus, the strength of the metal-DMF bonds is weakened with increasing number of chloride ions within the $[CuCl_n]^{(2-n)+}$ complex.[8]

In the present work, complex formation equilibria between copper(II) and chloride ions have been calorimetrically studied in various AN-DMF mixtures. Heats of solution of anhydrous $CuCl_2$ crystals have also been measured in the AN-DMF mixtures. Thermodynamic behavior of formation of $[CuCl_n]^{(2-n)+}$ (n=1—4) in the AN-DMF mixtures will be discussed in connection with the change in solvation of the metal ion and the complexes with varying solvent compositions.

Experimental

Reagent. All chemicals used were of reagent grade. Methods of preparation and purification of the chemicals were the same as those described in previous papers.[1,2]

Measurements. Calorimetric measurements were carried out in a thermostated bath controlled at (25.000±0.007) °C placed in a room thermostated at (25.0±0.2) °C.

All solutions used for calorimetric measurements contained 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ as a constant ionic medium. In each calorimetric measurement, 100 cm^3 of a copper(II) perchlorate solution of a given solvent composition was placed in a Dewar vessel filled with nitrogen gas and prevented from moisture with a P_2O_5 guard-tube, and then, was titrated with a 0.2 mol dm^{-3} $(C_2H_5)_4NCl$ solution of the same solvent composition. Concentrations of copper(II) perchlorate in initial test solutions were varied in the range 5—30 mmol dm^{-3}. Heat evolved at each titration point was measured in the range −5—5 J with a certainty ±0.05 J. Since heats of dilution of chloride ions in any AN-DMF mixture examined were found to be negligible by separate experiments, they were neglected in the course of the data treatments of heats measured.

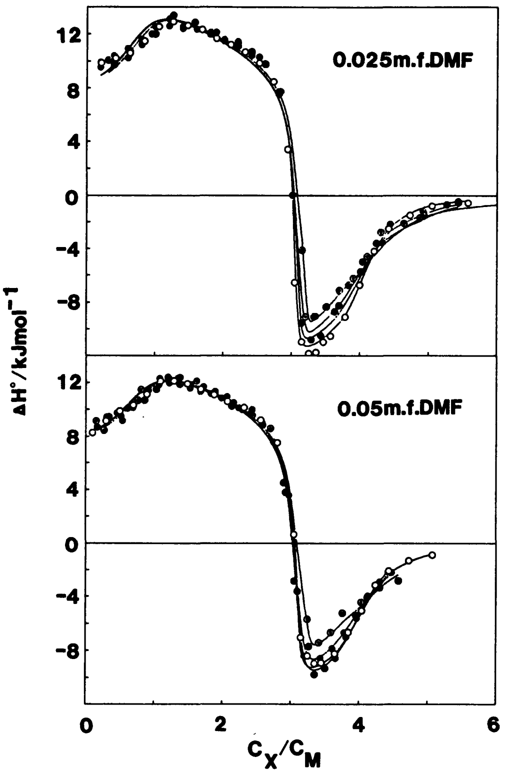

Fig. 1. Calorimetric titration curves of copper(II) chloride solutions in the AN-DMF mixtures of 0.025 and 0.05 mole fraction DMF containing 0.2 mol dm^{-3} $(C_2N_5)_4NClO_4$. Initial concentrations of copper(II) perchlorate (C_M/mol dm^{-3}): 4.55 (⊙), 7.14 (◎), 10.19 (●), and 19.25 (○) in the 0.025 mole fraction DMF mixture, and 6.05 (⊙), 11.83 (●), 20.48 (○), and 26.37 (◎), in the 0.05 mole fraction DMF mixture.

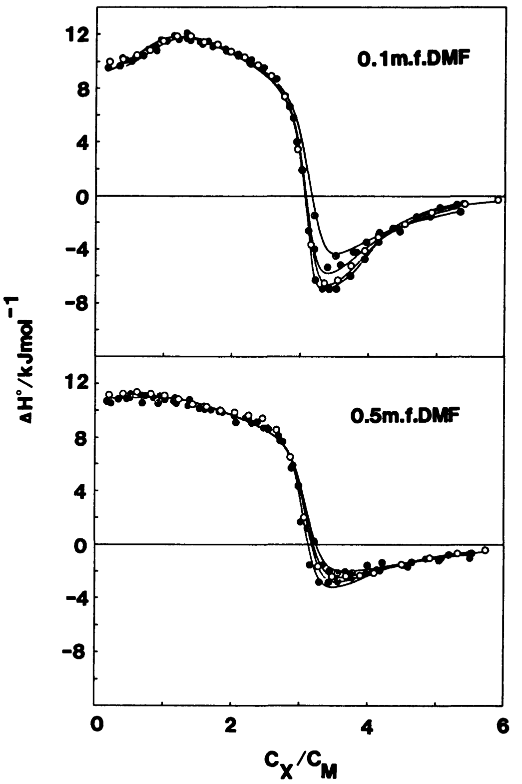

Fig. 2. Calorimetric titration curves of copper(II) chloride solutions in the AN-DMF mixtures of 0.1 and 0.5 mole fraction DMF containing 0.2 mol dm^{-3} $(C_2N_5)_4NClO_4$. Initial concentrations of copper(II) perchlorate (C_M/mol dm^{-3}): 4.59 (⊙), 10.69 (◎), 20.50 (○), and 29.23 (●) in the 0.1 mole fraction DMF mixture and 8.87 (⊙), 13.75 (◎), 19.81 (○), and 29.94 (●) in the 0.5 mole fraction DMF mixture.

Heats of solution of anhydrous $CuCl_2$ crystals were measured in the same AN-DMF mixtures as those used for the calorimetric titrations, but the mixtures involved no ionic medium, and the enthalpies $\Delta H^\circ_s(Cu^{2+},2Cl^-)$ and $\Delta H^\circ_s(CuCl_2)$ for the reactions, $CuCl_2(c)=Cu^{2+}(s)+2Cl^-(s)$ and $CuCl_2(c)=CuCl_2(s)$, respectively, were evaluated, where c and s stand for the crystalline and solution states, respectively.

Both titration and solution calorimetric measurements were carried out by using fully automatic on-line systems developed in our laboratory.[9-11]

Analysis of Calorimetric Data. The analytical method used for the calorimetric titration data was the same as that described in previous papers.[1,2]

The enthalpy of solution $\Delta H^\circ_{s,obsd}$ ($=-q_s/m$, where q_s and m denote the heat of solution measured and the number of moles of $CuCl_2$ dissolved, respectively) varied with the salt concentration in a solvent mixture because of the complex formation equilibria between copper(II) and chloride ions in the solvent. Therefore, the enthalpies $\Delta H^\circ_s(Cu^{2+},2Cl^-)$ and $\Delta H^\circ_s(CuCl_2)$ of solution were obtained by using the measured enthalpy of solution $\Delta H^\circ_{s,obsd}$ and the formation constants and enthalpies of formation of $[CuCl_n]^{(2-n)+}$ in each AN-DMF mixture as follows:

$$\Delta H^\circ_s(Cu^{2+},2Cl^-) = \Delta H^\circ_{s,obsd} - \sum_n \alpha_n \Delta H^\circ_{\beta n}, \quad (1)$$

$$\Delta H^\circ_s(CuCl_2) = \Delta H^\circ_s(Cu^{2+},2Cl^-) + \Delta H^\circ_{\beta 2}, \quad (2)$$

where α_n denotes the mole fraction of the $[CuCl_n]^{(2-n)+}$ complex. The α_n (n=1—4) values in a given solvent mixture were calculated in each measurement by knowing the formation constants of the $[CuCl_n]^{(2-n)+}$ (n=1—4) complexes and the total concentration of $CuCl_2$ dissolved in the solvent mixture.

Results and Discussion

Calorimetric titration curves in AN-DMF mixtures of 0.025, 0.05, 0.1, and 0.5 mole fraction DMF examined are illustrated in Figs. 1 and 2. In each solvent mixture, enthalpies ΔH° ($=-q/(vC_{X,tit})$ where v and $C_{X,tit}$ stand for the volume of an aliquot of the titrant added and the concentration of chloride ion in the titrant, respectively) were plotted against the ratio C_X/C_M in the test solution at each titration point.

As seen in Figs. 1 and 2, the ΔH° value was positive in the range $C_X/C_M<3$ but was turned to negative in the range $C_X/C_M>3$ in all the AN-DMF mixtures examined. The trend in the variation of ΔH° is similar to that in pure DMF, but different from that in pure AN where the ΔH° value is negative over the whole range of C_X/C_M.[2] Calorimetric titration curves in the 0.5 mole fraction DMF mixture were essentially the same as

Table 1. The Least-Squares Refinement of Formation Constants, β_n/mol^{-n}dm^{3n}, and Enthalpies, $\Delta H^\circ_{\beta n}$/kJ mol^{-1}, of Formation of Copper(II) Chloro Complexes in Acetonitrile-*N*,*N*-Dimethylformamide Mixtures Containing 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ as a Constant Ionic Medium at 25 °C

	DMF content/mole fraction			
	0.025	0.05	0.1	0.5
log β_1	6.7(0.4)	6.2(0.2)	5.9(0.1)	6.0(0.1)
log β_2	12.2(0.7)	11.4(0.4)	10.8(0.3)	10.9(0.1)
log β_3	18.4(1.2)	16.9(0.5)	15.8(0.4)	15.2(0.4)
log β_4	21.4(1.2)	19.7(0.5)	18.4(0.4)	17.3(0.4)
$\Delta H^\circ_{\beta 1}$	8.7(0.3)	8.3(0.2)	9.2(0.1)	10.9(0.1)
$\Delta H^\circ_{\beta 2}$	37.1(5)	29.9(2)	26.7(1)	22.2(0.2)
$\Delta H^\circ_{\beta 3}$	31.2(0.2)	29.9(0.2)	30.2(0.1)	30.0(0.2)
$\Delta H^\circ_{\beta 4}$	18.7(0.3)	18.8(0.2)	20.9(0.2)	23.5(0.2)
NP[a]	95	99	94	94
U[b]	1.67	1.29	0.84	1.51

Values in parentheses refer to standard deviations. a) The number of data points. b) The error-square sum.

those in pure DMF.[1] However, the titration curve noticeably changed with further decreasing the DMF content, i.e., the ΔH° values became more positive in the range $C_X/C_M=1$—2, but more negative in the range $C_X/C_M=3$—4 in the AN-DMF mixtures of lower DMF contents.

Calorimetric data in any AN-DMF mixture examined, as well as those in pure AN and DMF, were well explained in terms of the formation of $[CuCl_n]^{(2-n)+}$ (n=1—4). The formation constants and enthalpies of formation of the complexes obtained in each mixture are summarized in Table 1. As illustrated by the solid lines in Figs. 1 and 2, theoretical curves calculated by using the constants in Table 1 well reproduced the experimental points in each AN-DMF mixture examined.

Formation of the $[CuCl_4]^{2-}$ Complex. The $[CuCl_4]^{2-}$ complex is not solvated in the first solvation sphere of the metal ion in AN and in DMF.[1,2,8] The solvation energy of chloride ion in AN does not significantly differ from that in DMF because these solvents have a relatively poor acceptor property.[5] Consequently, the energy of formation of $[CuCl_4]^{2-}$ mainly depends on the solvation energy of the metal ion, especially in its first solvation sphere, in these solvents.

Thermodynamic quantities for the overall reaction, $Cu^{2+}+4Cl^-=[CuCl_4]^{2-}$, in the AN-DMF mixtures are summarized in Table 2, together with those in AN and in DMF for comparison. As seen in Table 2, the $\Delta G^\circ_{\beta 4}$, $\Delta H^\circ_{\beta 4}$, and $\Delta S^\circ_{\beta 4}$ values even in the acetonitrile-rich AN-DMF mixtures, such as the 0.025 mole fraction DMF mixture, were remarkably different from those in AN. Particularly, the $\Delta H^\circ_{\beta 4}$ value drastically changed from negative in pure AN to positive in the mixtures. Besides, the $\Delta S^\circ_{\beta 4}$ values in all the AN-DMF mixtures examined were much larger than those in AN and in DMF.

Table 2. Thermodynamic Quantities, $\Delta G^\circ_{\beta 4}$/kJ mol^{-1}, $\Delta H^\circ_{\beta 4}$/kJ mol^{-1}, and $\Delta S^\circ_{\beta 4}$/J K^{-1} mol^{-1}, for the Overall Reaction, $Cu^{2+}+4Cl^-=[CuCl_4]^{2-}$, in Acetonitrile, in *N*,*N*-Dimethylformamide and in Their Mixtures Containing 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ as a Constant Ionic Medium at 25 °C

	DMF content/mole fraction					
	0.0[a]	0.025	0.05	0.1	0.5	1.0[b]
$\Delta G^\circ_{\beta 4}$	−144.1	−122.1	−112.5	−105.3	−98.8	−96.2
$\Delta H^\circ_{\beta 4}$	−54.5	18.7	18.8	20.9	23.5	19.2
$\Delta S^\circ_{\beta 4}$	300	473	441	423	410	387

a) 0.1 mol dm^{-3} $(C_2H_5)_4NClO_4$ ionic medium, Ref. 2.
b) Ref. 1.

Table 3. Thermodynamic Quantities, log(K_n/mol^{-1}dm^3), ΔG°_n/kJ mol^{-1}, ΔH°_n/kJ mol^{-1}, and ΔS°_n/J K^{-1} mol^{-1}, for the Stepwise Reaction, $[CuCl_{n-1}]^{(3-n)+}+Cl^-=[CuCl_n]^{(2-n)+}$ (n=1—4), in Acetonitrile-*N*,*N*-Dimethylformamide Mixtures Containing 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ as a Constant Ionic Medium at 25 °C

	DMF content/mole fraction					
	0.0[a]	0.025	0.05	0.1	0.5	1.0[b]
log K_1	9.7	6.7	6.2	5.9	6.0	6.8
log K_2	8.0	5.5	5.2	4.9	4.9	4.5
log K_3	4.9	6.1	5.5	5.0	4.3	4.0
log K_4	2.9	3.0	2.9	2.6	2.2	1.5
ΔG°_1	−55.3	−38.3	−35.5	−33.8	−34.5	−38.8
ΔG°_2	−45.4	−31.5	−29.5	−28.1	−27.8	−25.9
ΔG°_3	−28.2	−35.0	−31.3	−28.5	−24.3	−22.8
ΔG°_4	−16.3	−17.3	−16.4	−14.9	−12.3	−8.8
ΔH°_1	−11.7	8.8	8.3	9.2	10.9	10.3
ΔH°_2	−5.0	28.4	21.6	17.5	11.3	9.7
ΔH°_3	−4.4	−5.9	0.0	3.5	7.8	7.3
ΔH°_4	−34.3	−12.5	−11.1	−9.3	−6.5	−8.1
ΔS°_1	147	158	147	144	152	165
ΔS°_2	135	201	171	153	131	120
ΔS°_3	80	98	105	107	107	101
ΔS°_4	−61	16	18	19	20	2

a) 0.1 mol dm^{-3} $(C_2H_5)_4NClO_4$ ionic medium, Ref. 2.
b) Ref. 1.

The thermodynamic quantities for the reaction, $[Cu(dmf)_4]^{2+}+4Cl^-=[CuCl_4]^{2-}+4dmf$, in AN can be calculated by combining those for two reactions, $Cu^{2+}+4Cl^-=[CuCl_4]^{2-}$ and $Cu^{2+}+4dmf=[Cu(dmf)_4]^{2+}$,[7] in the solvent. The enthalpy $\Delta H^{\circ *}_{\beta 4}$ and entropy $\Delta S^{\circ *}_{\beta 4}$ values thus calculated are 19.1 kJ mol^{-1} and 409 J K^{-1} mol^{-1}, respectively, which may be compared with the $\Delta H^\circ_{\beta 4}$ and $\Delta S^\circ_{\beta 4}$ values in the AN-DMF mixtures. The result indicates that a large difference of the $\Delta H^\circ_{\beta 4}$ and $\Delta S^\circ_{\beta 4}$ values found in the AN-DMF mixtures from those in pure AN may mainly be interpreted in terms of the preferential solvation of copper(II) ion with four DMF molecules in the mixtures.

Stepwise Formation of $[CuCl_n]^{(2-n)+}$ (n=1—4). Thermodynamic quantities, log(K_n/mol^{-1}dm^3), ΔG°_n/kJ mol^{-1}, ΔH°_n/kJ mol^{-1}, and ΔS°_n/J K^{-1} mol^{-1}, for the stepwise reaction, $[CuCl_{n-1}]^{(3-n)+}+Cl^-=[CuCl_n]^{(2-n)+}$ (n=1—4), are summarized in Table 3. Distribution of species

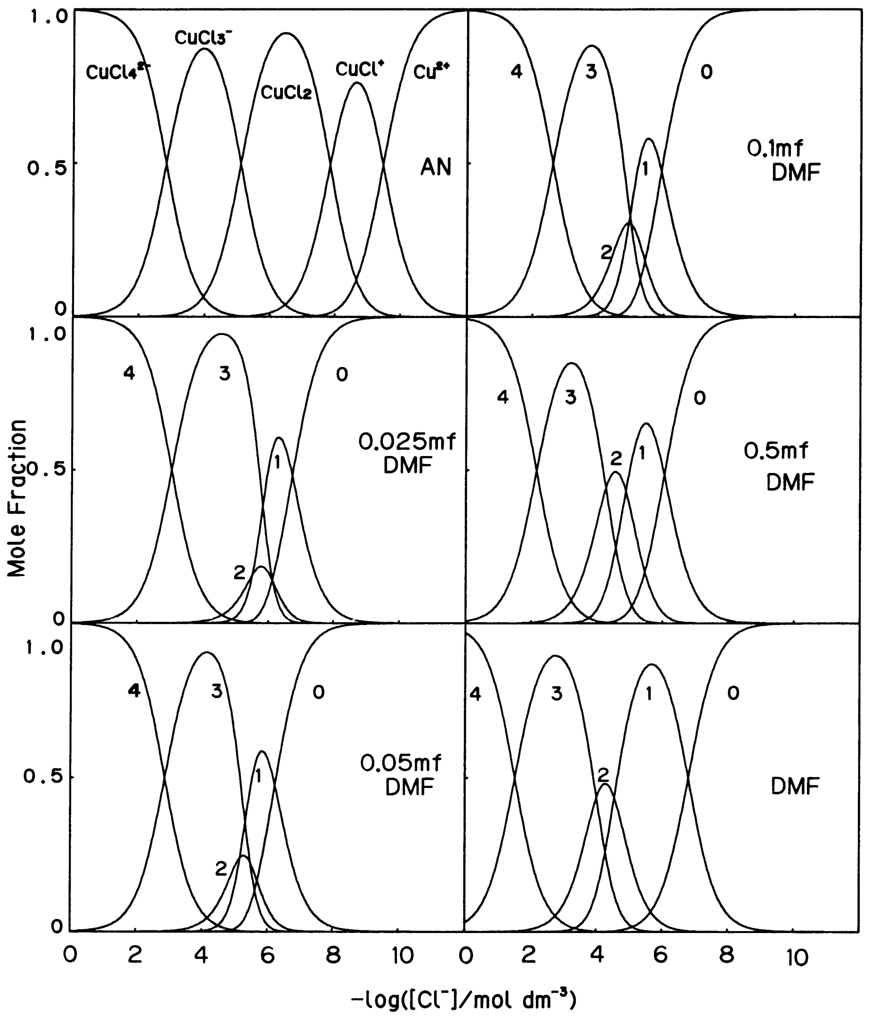

Fig. 3. Distribution curves of the copper(II) chloro complexes in various AN–DMF mixtures containing 0.2 mol dm^{-3} $(C_2N_5)_4NClO_4$ at 25 °C.

calculated by using the formation constants in each AN–DMF mixture examined is depicted in Fig. 3, together with those in the pure solvents for comparison.

The ΔH°_1 and ΔS°_1 values were both positive and practically kept constant in all the mixtures examined. The ΔH°_1 value in any mixture was more positive by ca. 20 kJ mol^{-1} than that in pure AN, the magnitude is about one fourth of the overall enthalpy of formation of $[Cu(dmf)_4]^{2+}$ in AN.7) It is thus plausible that one DMF molecule within $[Cu(dmf)_4]^{2+}$ is replaced with a chloride ion and $[CuCl(dmf)_3]^+$ is formed.

The ΔH°_2 and ΔS°_2 values became markedly positive in the AN–DMF mixtures of low DMF contents. The result indicates that the desolvation of DMF molecules from $[CuCl(dmf)_3]^+$ takes place in a different manner in each mixture depending on the solvent composition. On the other hand, the ΔH°_3 value became less positive with lowering DMF contents in the mixtures and the $(\Delta H^\circ_2+\Delta H^\circ_3)$ value was practically independent of the solvent composition. The result indicates that total number of DMF molecules desolvating at the second and third steps may be kept constant in all the mixtures examined. As discussed later, the $[CuCl_3(dmf)]^-$ species is expected to be present in all the AN–DMF mixtures examined. Therefore, two DMF molecules may be liberated at the second and third consecutive steps, but the desolvating scheme depends on the solvent composition in the mixtures. We propose:

$$[CuCl(dmf)_3]^+ + Cl^- = [CuCl_2(dmf)_2] + dmf, \tag{3}$$

$$[CuCl_2(dmf)_2] + Cl^- = [CuCl_3(dmf)]^- + dmf, \tag{4}$$

in a mixture of a high DMF content, while in a mixture of a relatively low DMF content,

$$[CuCl(dmf)_3]^+ + Cl^- = [CuCl_2(dmf)] + 2dmf, \tag{5}$$

$$[CuCl_2(dmf)] + Cl^- = [CuCl_3(dmf)]^-. \tag{6}$$

Accordingly, the dichlorocopper(II) complex may be solvated with one or two DMF molecules in the first coordination sphere of the metal ion, and thus, an equilibrium as represented by reaction 7 is established between the two solvate species of the dichloro

Table 4. Enthalpies of Solution, ΔH°_s/kJ mol^{-1}, of Anhydrous Copper(II) Chloride Salt in Various Acetonitrile-*N*,*N*-Dimethylformamide Mixtures at 25 °C

DMF content mole fraction	$\Delta H^\circ_{s,obsd}$	$\Delta H^\circ_s(CuCl_2)$	$\Delta H^\circ_s(Cu^{2+}, 2Cl^-)$
0.0	−15.9	−15.9	0.6
0.025	−38.0	−24.3	−61.3
0.05	−41.9	−34.2	−64.1
0.1	−42.5	−37.0	−63.7
0.5	−51.5	−50.5	−72.7
1.0	−55.3	−54.7	−74.6

complex,

$$[CuCl_2(dmf)] + dmf = [CuCl_2(dmf)_2], \tag{7}$$

and the equilibrium shifts depending on the DMF content in the AN–DMF mixtures.

The ΔH°_4 value was negative in any AN–DMF mixture examined and became slightly more negative with lowering DMF contents in the mixtures, but it remained much less negative than that in pure AN. The ΔS°_4 value was positive and was practically independent of the solvent composition in all the mixtures examined, while the ΔS°_4 value in AN was largely negative. The result suggests that one DMF molecule still coordinates to copper(II) ion within the trichlorocuprate(II) complex and $[CuCl_3(dmf)]^-$ is formed in all the mixtures.

Enthalpies of Solution of Anhydrous $CuCl_2$ Crystal. Copper(II) chloride dissolved in an AN–DMF mixture is mostly associated to form various chloro complexes of Cu(II), the distribution of which can be calculated by knowing the formation constants of the complexes and the total concentration of $CuCl_2$ dissolved in a solution. Therefore, by using the procedure described in the Experimental section, the enthalpies $\Delta H^\circ_s(Cu^{2+}, 2Cl^-)$ and $\Delta H^\circ_s(CuCl_2)$ of solution have been determined in various AN–DMF mixtures, the former being the sum of enthalpies of solution of relevant ions and the latter the enthalpy of the neutral complex. The results are summarized in Table 4 and also depicted in Fig. 4.

Although the enthalpies of transfer of both copper(II) and chloride ions from AN to any AN–DMF mixture have not been known, the change in $\Delta H^\circ_s(Cu^{2+}, 2Cl^-)$ with varying solvent compositions may mainly reflect the change in enthalpy of solvation of copper(II) ion because the acceptor properties (the property of solvating anions) of AN and DMF are weak and not appreciably different.

As seen in Table 4, the $\Delta H^\circ_s(Cu^{2+}, 2Cl^-)$ values in all the mixtures examined were largely negative. They are compared with the value in pure DMF, but are very different from the value in pure AN. This also indicates that copper(II) ion is preferentially solvated with DMF molecules in a wide range of the solvent composition of the AN–DMF mixtures.

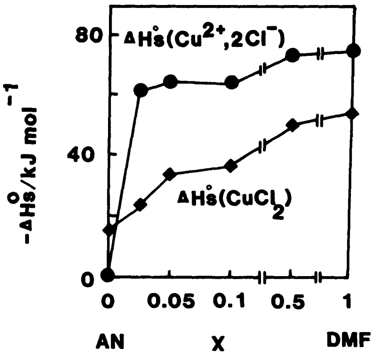

Fig. 4. Variations of $\Delta H^\circ_s(Cu^{2+}, 2Cl^-)$ and $\Delta H^\circ_s(CuCl_2)$ with mole fraction *x* of DMF in the AN–DMF mixtures.

The $\Delta H^\circ_s(CuCl_2)$ value in the 0.025 mole fraction DMF mixture was close to the value in pure AN, but the value in the 0.5 mole fraction DMF mixture was close to that in pure DMF as seen in Table 4. The values in the 0.05 and 0.1 mole fraction DMF mixture were laid just in the middle of the values in AN and in DMF. The variation of $\Delta H^\circ_s(CuCl_2)$ with solvent composition indicates that solvation of $[CuCl_2]$ with DMF molecules markedly weakens in an AN–DMF mixture of a low DMF content. Therefore, we concluded that the $[CuCl_2]$ complex was not markedly preferentially solvated with DMF molecules in contrast to copper(II) ion in the AN–DMF mixtures. This is not unexpected, considering that an electron donation from the ligands to the central metal ion within $[CuCl_2]$ may reduce the acceptor ability of copper(II) ion to lead to a weakened interaction of the metal ion with DMF molecules. The conclusion obtained here is also consistent with the result obtained in a preceding section that the ΔH°_2 value of stepwise formation of $[CuCl_2]$ became more positive with lowering DMF contents in the AN–DMF mixtures.

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as a constant ionic medium at 25 °C were −41.2, −73.6 kJ mol^{-1}, and −109 J K^{-1} mol^{-1}, respectively.

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