Effect of 2,2′-Bipyridine on Nickel(II)-Halide Interactions within Their Ternary Complexes in *N,N*-Dimethylformamide

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Synopsis. The formation of ternary (2,2′-bipyridine)-bromonickel(II) complexes has been studied by calorimetry in *N,N*-dimethylformamide containing 0.16 mol dm^{-3} $(C_2H_5)_4NClO_4$ as a constant ionic medium at 25 °C. The data are well explained in terms of the formation of $[NiBr(bpy)]^+$ and $[NiBr(bpy)_2]^+$ (bpy=2,2′-bipyridine), and their formation constants, enthalpies and entropies were determined. It is elucidated that the affinities of Br^- as well as Cl^- ions to $[Ni(bpy)]^{2+}$ and $[Ni(bpy)_2]^{2+}$ are enhanced almost to the same extent over Ni^{2+}. The enhancement is ascribed mainly to an increase in entropies upon complexation in both Ni^{II}–Cl^-–bpy and Ni^{II}–Br^-–bpy systems.

Affinities of halide ions to a metal ion change depending on the solvent.[1] Ligating anions or molecules to a metal ion in ternary systems also influence the affinities of halide ions.[2] In the ternary Ni^{II}–Cl^-–bpy (bpy=2,2′-bipyridine) system the formation of $[NiCl(bpy)]^+$, $[NiCl_2(bpy)]$, $[NiCl(bpy)_2]^+$, and $[NiCl_2(bpy)_2]$ has been proposed in DMF.[3] It is found that the log K_1 value for the formation of $[MCl]^+$ is appreciably larger for M=$[Ni(bpy)]^{2+}$ or $[Ni(bpy)_2]^{2+}$ than for Ni^{2+}. Furthermore, the enhanced complexation is essentially due to the increased entropies and the corresponding enthalpies remain rather constant. Relative affinities among halide ions to nickel(II) ion may be of interest in view of hard and soft acids and bases. Therefore, we examined the complexation equilibria in the Ni^{II}–Br^-–bpy system in DMF by calorimetry at 25 °C, and the result was compared with that in the Ni^{II}–Cl^-–bpy system.

Results and Discussion

Calorimetric titration curves obtained in the ternary Ni^{II}–Br^-–bpy system are depicted in Fig. 1. The heat of reaction q measured at each titration point is normalized with the volume of the titrant added δv and the concentration of the ligand ions in the titrant $C_{X,tit}$, and the term $-q/(\delta v C_{X,tit})$ is plotted against C_X/C_M, where C_X and C_M denote the total concentrations of the bromide and metal ions, respectively, in solution. As seen in Table 1 the formation of various sets of ternary $[NiBr_p(bpy)_q]^{(2-p)+}$ complexes was assumed along with the relevant binary complexes. Analyzed on the basis of the known thermodynamic parameters for the binary 2,2′-bipyridine[3] and bromo[4] complexes of nickel(II), the titration curves in Fig. 1 are finally explained in terms of the formation of $[NiBr(bpy)]^+$ and $[NiBr(bpy)_2]^+$ (case A in Table 1). The solid lines in Fig. 1, calculated using the constants for case A in Table 1, well reproduce the experimental points. It is elucidated that the formation of $[NiBr_2(bpy)]$ and $[NiBr_2(bpy)_2]$ is practically negligible in contrast to that of the corresponding $[NiCl_2(bpy)]$ and $[NiCl_2(bpy)_2]$ complexes.[3] It is also noted that the formation of $[NiBr_2]$ is virtually negligible in DMF.[4]

In Table 2 are compared the thermodynamic parameters for the formation of $[MX]^+$ (X=Cl, Br and M=Ni^{2+}, $[Ni(bpy)]^{2+}$, $[Ni(bpy)_2]^{2+}$). We see from Table 2 that for $[Ni(bpy)]^{2+}$ as well as $[Ni(bpy)_2]^{2+}$ the log K_1(Br) value is smaller than the log K_1(Cl) value, and the decrement is to an almost similar extent to that for Ni^{2+}. The ΔH_1°(Br) value is larger than the ΔH_1°(Cl) value for $[Ni(bpy)]^{2+}$ as well as $[Ni(bpy)_2]^{2+}$, and the increment is also to an almost similar extent to the value for Ni^{2+}. On the othen hand, practically the

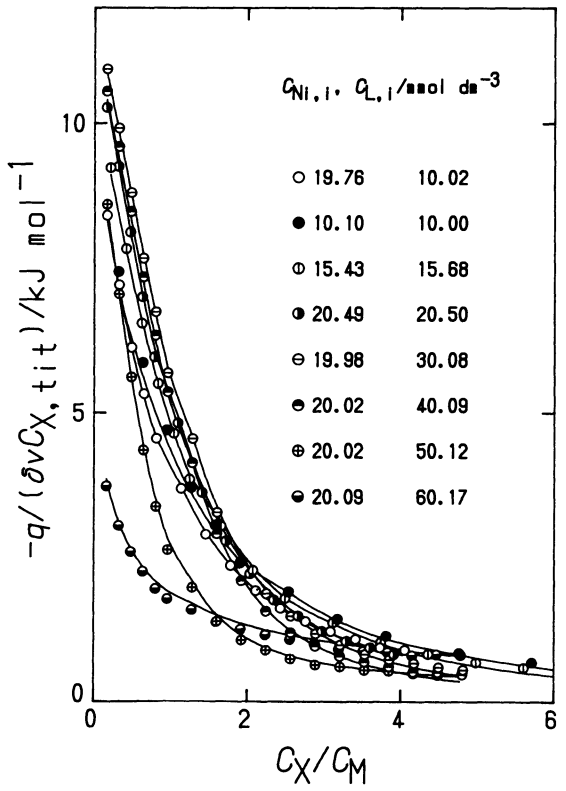

Fig. 1. Calorimetric titration curves obtained for the Ni^{II}–Br^-–bpy system in *N,N*-dimethylformamide containing 0.16 mol dm^{-3} $(C_2H_5)_4NClO_4$ at 25 °C. The concentrations of Ni^{2+} ion and 2,2′-bipyridine in initial test solutions, $C_{Ni,i}$ and $C_{L,i}$/mmol dm^{-3}, are given.

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Table 1. Least-Squares Refinement of Overall Formation Constants, $\log(\beta_{1pq}/\mathrm{mol}^{-(p+q)}\,\mathrm{dm}^{3(p+q)})$ and Enthalpies, $\Delta H^\circ_{\beta 1pq}/\mathrm{kJ\ mol}^{-1}$, of $[NiBr_p(bpy)_q]^{(2-p)+}$ (bpy=2,2′-bipyridine) in *N,N*-Dimethylformamide Containing 0.16 mol dm^{-3} $(C_2H_5)_4NClO_4$ at 25 °C[a]

	Case A	Case B	Case C
$\log\beta_{111}$	7.80(0.04)	8.00(0.09)	7.8(0.14)
$\log\beta_{112}$	13.39(0.03)	13.38(0.03)	13.39(0.03)
$\log\beta_{121}$	—	2.65(0.24)	7.1[b]
$\log\beta_{122}$	—	—	5.3(0.5)
$\Delta H^\circ_{\beta 111}$	−11.6(0.9)	−15.7(1.4)	−12.2(3.4)
$\Delta H^\circ_{\beta 112}$	−48.1(0.4)	−47.9(0.4)	−47.9(0.6)
$\Delta H^\circ_{\beta 121}$	—	very large	40.5[b]
$\Delta H^\circ_{\beta 122}$	—	—	very large
U[c]	0.0717	0.0535	0.0647
R[d]	0.0305	0.0264	0.0290

a) Values in parentheses refer to 3σ. The total number of calorimetric data points is 132. The assumed complexes are [111] and [112] in case A, [111], [112], and [121] in case B, and [111], [112], [121], and [122] in case C. The overall formation constant and enthalpies of formation of the relevant binary complexes, $[NiBr]^+$ ($\log\beta$=1.20, ΔH°=17.5 kJ mol^{-1}), $[Ni(bpy)]^{2+}$ (5.90, −31.1), $[Ni(bpy)_2]^{2+}$ (11.18, −63.8), $[Ni(bpy)_3]^{2+}$ (15.43, −92.2) were fixed as known parameters. b) Very large standard deviation. c) Error-square sum. d) The Hamilton R factor.

Table 2. Stepwise Formation Constants, $\log(K_1/\mathrm{mol}^{-1}\,\mathrm{dm}^3)$, Enthalpies, $\Delta H_1^\circ/\mathrm{kJ\ mol}^{-1}$, and Entropies, $\Delta S_1^\circ/\mathrm{J\ K}^{-1}\,\mathrm{mol}^{-1}$, for the reaction, $M^{2+}+X^-=[MX]^+$, where X=Cl or Br, and M=Ni, [Ni(bpy)], or $[Ni(bpy)_2]$ (bpy=2,2′-bipyridine), in *N,N*-Dimethylformamide at 25 °C

	X	Ni^{2+}	$[Ni(bpy)]^{2+}$	$[Ni(bpy)_2]^{2+}$
$\log K_1$	Cl	2.85[a]	3.68[b]	3.77[b]
	Br	1.20[c]	1.90	2.21
ΔH_1°	Cl	8.6[a]	8.4[b]	7.9[b]
	Br	17.5[c]	19.5	15.7
ΔS_1°	Cl	83[a]	99[b]	99[b]
	Br	82[c]	102	95

a) Ref. 6. b) Ref. 3. c) Ref. 4.

same ΔS_1° values for Cl and Br are found for all the M ions. These results imply that the Ni^{II}–X^- (X=Cl, Br) interactions are not appreciably influenced by the coordination of 2,2′-bipyridine molecules to the nickel(II) ion, in other words, the coordination of 2,2′-bipyridine molecules to nickel(II) ion does not change virtually the hard and soft nature of the nickel(II) ion.

With regard to the bromo complexes the $\log K_1$ value for $[Ni(bpy)]^{2+}$ is larger than that for Ni^{2+}. The value for $[Ni(bpy)_2]^{2+}$ is also larger than that for Ni^{2+}. The larger $\log K_1$ values are ascribed mainly to the increased entropies upon complexation, and the change in the corresponding enthalpies is rather small. The same conclusion has been obtained for X=Cl. Consequently, the entropy increase seems to be independent of the kind and nature of halide ions. Nickel(II) ion and its binary 2,2′-bipyridine complexes are solvated to form six-coordinated $[Ni(dmf)_6]^{2+}$, $[Ni(bpy)(dmf)_4]^{2+}$ and $[Ni(bpy)_2(dmf)_2]^{2+}$ in DMF. Therefore, a specific or steric intermolecular bpy–dmf interaction might occur in $[Ni(bpy)(dmf)_4]^{2+}$ and $[Ni(bpy)_2(dmf)_2]^{2+}$, which is expected to lead to the entropy increase for $[Ni(bpy)]^{2+}$ and $[Ni(bpy)_2]^{2+}$.

Experimental

Reagents. Chemicals used were prepared or purified as described elsewhere.[3]

Measurements. Calorimetric measurements were carried out using an on-line controlled calorimetry system.[5] Varying concentrations of nickel(II) perchlorate 2,2′-bipyridine solutions (40 cm^3) containing 0.16 mol dm^{-3} $(C_2H_5)_4NClO_4$ as a constant ionic medium were titrated with a 0.16 mol dm^{-3} $(C_2H_5)_4NBr$ solution. The detailed procedure of the measurements is described elsewhere.[3]

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