Solvation and Protonation of 1,10-Phenanthroline in Aqueous Dioxane Solutions

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Solvation and protonation of 1,10-phenanthroline (phen) have been studied by potentiometry and calorimetry in various aqueous dioxane solutions. Protonation reactions were studied in the mixtures (the dioxane content x=0—0.4 mole fraction) containing 0.3 mol dm^{-3} NaCl as a constant ionic medium at 25 °C. Potentiometric and calorimetric titration curves obtained in the range of $-\log[H^+]$=2—7 were well explained in terms of the formation of $Hphen^+$ and $H(phen)_2^+$, and the formation constants, enthalpies and entropies of formation of the species were determined. The formation constants of the both species gradually decreased with increasing x, and then the formation of $H(phen)_2^+$ became negligibly small at x>0.1, while the enthalpy and entropy of formation of $Hphen^+$ first decreased and then increased with increasing x and thus minima were found at x=0.05. Enthalpies of solution of anhydrous 1,10-phenanthroline were also determined in both neutral (x=0—1) and acidic (0.1 mol dm^{-3} HCl, x=0—0.4) aqueous dioxane solutions. By knowing enthalpies of solution of 1,10-phenanthroline in acidic solutions and of formation of $Hphen^+$ in the mixed solvents, enthalpies of solution of 1,10-phenanthroline in neutral solutions (ΔH_s°(phen)) were evaluated and compared with those directly obtained in the neutral solutions ($\Delta H_{s,\text{neutral}}^\circ$). A significant difference was found between ΔH_s°(phen) and $\Delta H_{s,\text{neutral}}^\circ$ in the range x<0.3, which could be ascribed to the formation of stacked species of 1,10-phenanthroline molecules, $(phen)_n$. The variation of ΔH_s°(phen) with x was explained in terms of the enhanced solvation of dioxane to phenanthroline molecules owing to breaking of the hydrophobic water structure around them. Solvent effects on the formation of $Hphen^+$ and $H(phen)_2^+$ were discussed in terms of different solvation behavior of 1,10-phenanthroline and proton with x.

Protonation reactions of 1,10-phenanthroline (phen) in aqueous solutions have so far been studied by potentiometry and calorimetry, and it has been reported that $Hphen^+$ and $H(phen)_2^+$ were formed in the range of $-\log[H^+]$=2—7 and H_2phen^{2+} was also found in a solution of $[H^+]$>1 mol dm^{-3}.[1-5]

A proton NMR study of 1,10-phenanthroline solutions containing various concentrations of hydrochloric acid also suggested the formation of $Hphen^+$ and $H(phen)_2^+$ and, in fact, the $Hphen \cdot ClO_4$ and $H(phen)_2 \cdot ClO_4$ crystals were isolated.[6]

Due to the hydrophobicity of aromatic rings of 1,10-phenanthroline, the solubility of the neutral species is low in water, but remarkably increases in organic solvents and also in aqueous organic mixtures. With this point of view, protonation reactions of 1,10-phenanthroline have been studied in various aqueous alcohol solutions.[7]

Solvent effects on protonation reactions of 1,10-phenanthroline is very different from those of amines and amino acids. The protonation constant of $Hphen^+$ decreases with increasing concentration of an organic component in aqueous organic solutions, in contrast to protonation constants of amino and carboxyl groups which are practically invariable and remarkably increases, respectively, in the solutions.

The formation of $H(phen)_2^+$ and different solvent effects on the formation of $Hphen^+$ from those on the formation of protonated amines or amino acids suggested an importance of solvation at aromatic rings of 1,10-phenanthroline in the course of protonation reactions of 1,10-phenanthroline. In order to elucidate the solvation phenomenon of 1,10-phenanthroline, enthalpies of solution of anhydrous 1,10-phenanthroline were determined both in neutral aqueous dioxane solutions (x=0—1) and in acidic ones containing 0.1 mol dm^{-3} HCl (x=0—0.4). Thermodynamic quantities, ΔG_n°, ΔH_n°, and ΔS_n°, for protonation reactions of 1,10-phenanthroline in various aqueous dioxane solutions will be discussed in connection with changes in solvation of the neutral and protonated species.

Experimental

Reagents. All chemicals used were of reagent grade. *1,10-Phenanthroline monohydrate* was recrystallized three times from water and then dried in a vacuum desiccator over P_2O_5 to prepare anhydrous 1,10-phenanthroline. *Sodium hydroxide* was prepared by electrolysis of an aliquot of a sodium chloride solution under an atmosphere of nitrogen gas in a polyethylene bottle. *Hydrochloric acid* and *sodium chloride* of super special grade were used without further purification. *Dioxane* was dried with metallic sodium and then distilled.

Method of Measurements and Analysis of Data. All potentiometric and calorimetric measurements were carried out in thermostated baths at (25.00±0.02) °C and (25.000±0.007) °C, respectively, which were placed in a room thermostated at (25.0±0.2) °C.

Throughout potentiometric and calorimetric titrations, 0.3 mol dm^{-3} NaCl was used as an ionic medium, except for the 0.4 mole fraction dioxane-water mixture in which a lower ionic medium of *ca.* 0.05 mol dm^{-3} NaCl was used because of the phase separation in a solution of a higher salt concentration. In the course of potentiometric titrations,

values of $-\log[H^+]$ in solutions were measured by using a glass electrode and an Ag-AgCl electrode as reference over the range 2 to 7. In calorimetric titrations, 1,10-phenanthroline solutions were titrated with a hydrochloric acid solution of *ca.* 0.3 mol dm^{-3}. The method of measurements were similar to those described elsewhere.[8]

Enthalpies of solution of anhydrous 1,10-phenanthroline were measured by dissolving a given amount of crystals of the anhydrous species in either neutral or acidic (0.1 mol dm^{-3} HCl) aqueous dioxane solution in which no medium salt was contained. Procedures of the measurements and analysis of data were described in a previous paper.[9]

Results and Discussion

The formation curves experimentally obtained, $\bar{n}_{H,obsd}=(C_H-[H^+])/C_L$, where C_H and C_L denote the total concentrations of proton and 1,10-phenanthroline in the solution, respectively, at each point of titration are depicted in Fig. 1. We found that experimental points systematically deviated from the theoretical curve (curve A in Fig. 1) calculated by assuming the formation of only Hphen$^+$. Thus we assumed the formation of other species such as H(phen)$_2^+$ and H(phen)$_3^+$ which may be expected to be formed at $-\log[H^+]=4$—6. As shown in Table 1, the introduction of H(phen)$_2^+$ (case 2) significantly improved the error square sum, $U=\sum\{(C_{H,obsd}-C_{H,calcd})^2+(C_{L,obsd}-C_{L,calcd})^2\}$, while further introduction of H(phen)$_3^+$ (case 3) did not improve the result anymore. Experimental points well fell on the curve (curve B in Fig. 1) calculated by assuming the formation of Hphen$^+$ and H(phen)$_2^+$. Therefore, we concluded that the Hphen$^+$ and H(phen)$_2^+$ species were formed in the solutions under the present experimental conditions.

Table 1. The least-squares refinement of formation constants of H(phen)$_n^+$ in aqueous solution containing 0.3 mol dm^{-3} NaCl at 25 °C

Species	$\log\beta_n$		
	Case 1	Case 2	Case 3
Hphen$^+$	4.97(0.0061)	4.96(0.0032)	4.97(0.0025)
H(phen)$_2^+$	—	6.65(0.019)	6.63(0.10)
H(phen)$_3^+$	—	—	7.90(0.045)
U	8.3×10^{-7}	9.2×10^{-8}	9.1×10^{-8}

The values in parentheses refer to standard deviations.

Calorimetric titration curves are illustrated in Fig. 2 as the heat evolved, $\Delta H^\circ=q/vC_{H,tit}$, at the addition of a potion of a standard hydrochloric acid solution against the ratio C_H/C_L in the solution, where q, v, and $C_{H,tit}$ stand for heat measured and volume of the titrant added at each point of titration and concentration of hydrochloric acid in the titrant solution, respectively. The ΔH° curves obtained in the aqueous dioxane solutions depended on the ratio C_H/C_L, and the curves were well reproduced by assuming the formation of Hphen$^+$ and H(phen)$_2^+$ (the solid lines in Fig. 2).

The formation constants and enthalpies finally obtained by the least-squares procedure for the formation of Hphen$^+$ and H(phen)$_2^+$ in the aqueous dioxane solutions examined are summarized in Table 2. With increasing mole fraction of dioxane in the mixtures, the formation of H(phen)$_2^+$ became unfavorable and practically negligible in mixtures of $x>0.1$. It should

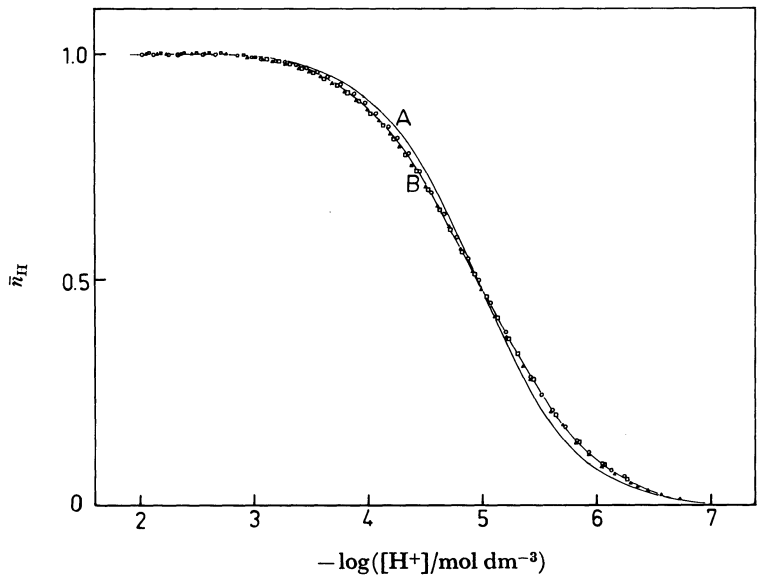

Fig. 1. Formation curves of protonated species of 1,10-phenanthroline (phen) in aqueous solution.
C_L(phen)/mmol dm^{-3}=7.215 (○), 10.84 (△), and 13.00 (□). The solid lines A and B were calculated in case 1 (Hphen$^+$ only) and case 2 (Hphen$^+$ and H(phen)$_2^+$), respectively.

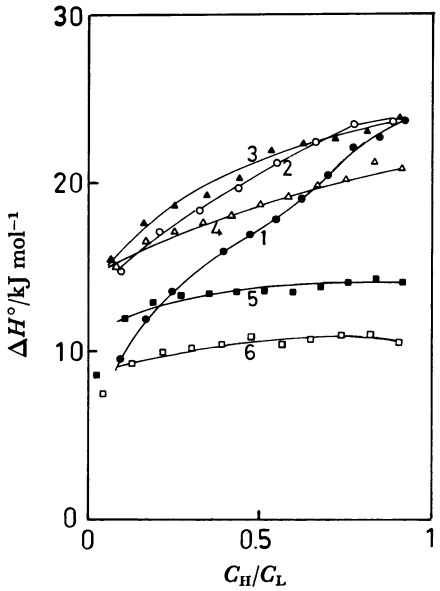

Fig. 2. Calorimetric titration curves of 1,10-phenanthroline aqueous dioxane solutions.
Curve 1: mole fraction of dioxane x=0.0; 2: 0.025; 3: 0.05; 4: 0.1; 5: 0.2; 6: 0.3. The solid lines show the curves calculated by using the constants obtained in Table 2.

be noted that the dependence of $\Delta H°$ on the ratio C_H/C_L became less pronounced with x in the mixtures (see Fig. 2). This reflected that the formation of $H(phen)_2^+$ became insignificant in the mixture of higher x.

The thermodynamic quantities, log (K_n/mol^{-1} dm^3), $\Delta G_n°$/kJ mol^{-1}, $\Delta H_n°$/kJ mol^{-1}, and $\Delta S_n°$/JK^{-1} mol^{-1}, for the stepwise reactions, $H(phen)_{n-1}^+$+phen=$H(phen)_n^+$ (n=1 and 2), are summarized in Table 3.

Enthalpies of solution of anhydrous 1,10-phenanthroline were determined in both neutral ($\Delta H°_{s,neutral}$, x=0—1) and acidic ($\Delta H°_{s,acid}$, x=0—0.4) aqueous dioxane solutions. In the neutral solvents, the formation of protonated species of 1,10-phenanthroline were negligible. In solutions involving 0.1 mol dm^{-3} HCl, 1,10-phenanthroline was fully converted into $Hphen^+$, but not into $H(phen)_2^+$ in such a highly acidic solution. Thus, the enthalpy of solution measured in an acidic solution at a given solvent composition was given as the sum of enthalpies of solution of 1,10-phenanthroline ($\Delta H_s°$(phen)) and of formation of $Hphen^+$ ($\Delta H_1°$), the latter value having been determined in the calorimetric titration experiment as described in the previous section. Thus $\Delta H_s°$(phen)

TABLE 2. THE FORMATION CONSTANTS, β_n/mol^{-n} dm^{3n}, AND ENTHALPIES, $\Delta H°_{\beta n}$/kJ mol^{-1}, FOR THE REACTION, $H^+ + nL = HL_n^+$; $\beta_n = [HL_n^+]/[H^+][L]^n$ (L=phen) IN AQUEOUS DIOXANE CONTAINING 0.3 mol dm^{-3} NaCl AT 25 °C

Concentration of dioxane / mole fraction	log β_1	log β_2	$\Delta H°_{\beta 1}$	$\Delta H°_{\beta 2}$
0	4.96(0.01)	6.65(0.06)	−16.6(0.3)	−34.3(1.4)
0.0125	4.83(0.02)	6.52(0.17)	—	—
0.025	4.71(0.02)	6.16(0.24)	−19.7(0.3)	−35.9(2.3)
0.05	4.57(0.02)	6.02(0.20)	−20.7(0.3)	−30.6(1.8)
0.1	4.33(0.01)	5.71(0.25)	−18.7(0.4)	−25.3(0.2)
0.2	4.10(0.01)	5.32(0.25)	−13.9(0.3)	—
0.3	3.86(0.01)	—	−10.7(0.2)	—
0.4	3.86(0.01)	—	−10.2(0.2)	—

The values in parentheses refer to three standard deviations.

TABLE 3. THE FORMATION CONSTANTS, K_n/mol^{-1} dm^3, AND THERMODYNAMIC QUANTITIES, $\Delta G_n°$/kJ mol^{-1}, $\Delta H_n°$/kJ mol^{-1}, AND $\Delta S_n°$/JK^{-1} mol^{-1}, FOR THE STEPWISE REACTION, $H(phen)_{n-1}^+ + phen = H(phen)_n^+$ (n=1 AND 2) IN DIOXANE-WATER MIXTURES CONTAINING 0.3 mol dm^{-3} NaCl AS A CONSTANT IONIC MEDIUM AT VARIOUS MOLE FRACTIONS x OF DIOXANE

x	$Hphen^+$				$H(phen)_2^+$			
	log K_1	$\Delta G_1°$	$\Delta H_1°$	$\Delta S_1°$	log K_2	$\Delta G_2°$	$\Delta H_2°$	$\Delta S_2°$
0.0	4.96	−28.3	−16.6	39	1.69	−9.6	−17.7	−27
0.0125	4.83	−27.6	—	—	1.69	−9.6	—	—
0.025	4.71	−26.9	−19.7	24	1.45	−8.3	−16.2	−27
0.05	4.57	−26.1	−20.7	18	1.45	−8.3	−9.9	−5
0.1	4.33	−24.7	−18.7	20	1.38	−7.4	−6.6	+4
0.2	4.01	−22.9	−13.9	30				
0.3	3.86	−22.0	−10.7	38				
0.4	3.86	−22.0	−10.2	40				

Table 4. Enthalpies of solution of 1,10-phenanthroline measured in acidic ($\Delta H^\circ_{s,acid}$/kJ mol^{-1}) and neutral ($\Delta H^\circ_{s,neutral}$/kJ mol^{-1}) aqueous dioxane solutions, and calculated enthalpies of solution of monomeric 1,10-phenanthroline (ΔH°_s(phen)/kJ mol^{-1}) in the mixtures

Dioxane content / mole fraction	$\Delta H^\circ_{s,acid}$	$\Delta H^\circ_{s,neutral}$	ΔH°_i	ΔH°_s(phen)	$\Delta H^\circ_{s,neutral} - \Delta H^\circ_s$(phen)
0.0	−11.6	−0.3	−16.6	5.0	−5.3
0.025	−10.2	—	−19.7	9.5	—
0.05	−9.4	3.9	−20.7	11.3	−7.4
0.10	−5.0	5.7	−18.7	13.7	−8.0
0.20	−0.6	11.3	−13.9	13.3	−2.0
0.30	−1.2	10.0	−10.7	9.5	0.5
0.40	0.2	10.8	−10.2	10.4	0.4
0.60		11.9			
0.70		11.4			
0.80		11.7			
0.90		13.4			
1.0		17.7			

was calculated according to Eq. 1.

$$\Delta H^\circ_s(\text{phen}) = \Delta H^\circ_{s,acid} - \Delta H^\circ_i \quad (1)$$

Values of ΔH°_s(phen), $\Delta H^\circ_{s,acid}$, and $\Delta H^\circ_{s,neutral}$ obtained in various aqueous dioxane solutions are summarized in Table 4.

Enthalpies of Solution of 1,10-Phenanthroline. If only monomeric 1,10-phenanthroline molecules were present in a neutral solution $\Delta H^\circ_{s,neutral}$ should be equal to ΔH°_s(phen). However, as seen in Fig. 3, ΔH°_s(phen) was appreciably different from $\Delta H^\circ_{s,neutral}$ in the dioxane-water mixtures of $x<0.3$. The difference may be ascribed to the formation of stacked neutral species of 1,10-phenanthroline, $(phen)_n$, in the neutral solvent mixtures, as suggested by an NMR study in water.[10] The value of $\Delta H^\circ_{s,neutral}$ was always positive but smaller than ΔH°_s(phen) in the mixtures of $x<0.3$, which suggested that the enthalpy of formation of the stacks should be negative if such stacks of 1,10-phenanthroline are formed in the mixtures. Negative enthalpies for the formation of stacked species were also reported for Methylene Blue in aqueous mixtures of various alcohols.[11]

The value of ΔH°_s (phen) was practically the same as $\Delta H^\circ_{s,neutral}$ in the dioxane-water mixtures at $x=0.3$ and 0.4, and the results suggested that the stacks did not form in the solutions due, probably, to destruction of the hydrogen-bonded structure of water in the bulk, which led to the decomposition of the hydrophobic hydration sphere around the aromatic rings of 1,10-phenanthroline. Observations by means of X-ray diffraction[12] suggested the destruction of the hydrogen-bonded structure of bulk water at $x>0.3$.

Values of ΔH°_s(phen) were obtained in aqueous dioxane solutions at $x=0$—0.4, but not in solutions at $x>0.4$ on account of experimental difficulties for determination of ΔH°_i and $\Delta H^\circ_{s,acid}$. However, since self-

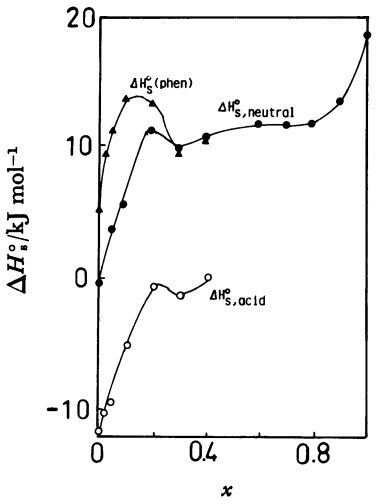

Fig. 3. Enthalpies of solution of 1,10-phenanthroline in neutral ($\Delta H^\circ_{s,neutral}$) and acidic ($\Delta H^\circ_{s,acid}$) solutions and ΔH°_s(phen) plotted against x.

stacking of 1,10-phenanthroline molecules was hardly expected in aqueous dioxane solutions at $x>0.4$ and, in fact, practically the same values of ΔH°_s(phen) as those of $\Delta H^\circ_{s,neutral}$ were found in the mixtures at $x=0.3$ and 0.4, we can reasonably assume that $\Delta H^\circ_s(\text{phen}) = \Delta H^\circ_{s,neutral}$ in aqueous dioxane solutions at $x>0.4$.

The value of ΔH°_s(phen) steeply increased with increasing x up to 0.1, and then slightly decreased in the range $x=0.1$—0.3. The sharp increase in ΔH°_s was also reported for the solution of 2,2′-bipyridyl in aqueous alcohol solutions with increasing alcohol content.[13] A further increase in x did not appreciably affect the ΔH°_s(phen) value until $x=0.8$. In the range $x>0.8$, ΔH°_s(phen) again steeply increased with x, and ΔH°_s(phen) in pure dioxane was more positive by about 13 kJ mol^{-1} than that in pure water. It is well known that the solubility of 1,10-phenanthroline markedly increases in organic solvents. Therefore,

the result that ΔH_s°(phen) was more endothermic in pure dioxane than in pure water indicated that the high solubility of 1,10-phenanthroline in dioxane was essentially owing to the contribution of a large entropy of solution of the species.

The variation of ΔH_s°(phen) in the range x=0—0.1 may be explained in terms of enhanced solvation of dioxane due to the breaking of the hydrophobic hydration structure around the aromatic rings of 1,10-phenanthroline molecules. A slight decrease of ΔH_s°(phen) in the range x=0.1—0.3 may be ascribed to the enhanced hydration of hydrophilic nitrogen atoms within 1,10-phenanthroline due to the breaking of the hydrogen-bonded water structure in the bulk. The enhancement of hydration of cations in aqueous dioxane solutions than in water has been suggested in a previous paper.[9]

The solvation structure of 1,10-phenanthroline with water at the sites of nitrogen atoms and with dioxane at the aromatic part may be practically remained unchanged in the range x=0.3—0.8, so that ΔH_s°(phen) was almost independent of solvent composition.

In solutions of the highest dioxane content x>0.8, water molecules solvating the nitrogen atoms within 1,10-phenanthroline may be replaced with dioxane molecules.

Solvent Effects on the Formation of Hphen$^+$.
The solvent effect on thermodynamic quantities for the formation of Hphen$^+$ was shown in Fig. 4, where the increments of ΔG_1°, ΔH_1°, and $T\Delta S_1^\circ$ in an aqueous dioxane solution from those in water, $\Delta\Delta G_1^\circ = \Delta G_1^\circ$(mix)$-\Delta G_1^\circ$(w), $\Delta\Delta H_1^\circ = \Delta H_1^\circ$(mix)$-\Delta H_1^\circ$(w), and $T\Delta\Delta S_1^\circ = T\Delta S_1^\circ$(mix)$-T\Delta S_1^\circ$(w), are plotted against x in the range x<0.4.

$\Delta\Delta G_1^\circ$ monotonously increased with increasing x, while $\Delta\Delta H_1^\circ$ and $T\Delta\Delta S_1^\circ$ first decreased and then increased after passing through minima at x=0.05 with increasing x. The change in $\Delta\Delta H_1^\circ$ can be expressed in terms of enthalpies of transfer, $\Delta H_t^\circ = \Delta H_s^\circ$(mix)$-\Delta H_s^\circ$(w), of the related species from water to the dioxane-water mixtures as follows:

$$\Delta\Delta H_1^\circ = \Delta H_t^\circ(\text{Hphen}^+) - \Delta H_t^\circ(\text{H}^+) - \Delta H_t^\circ(\text{phen}). \quad (2)$$

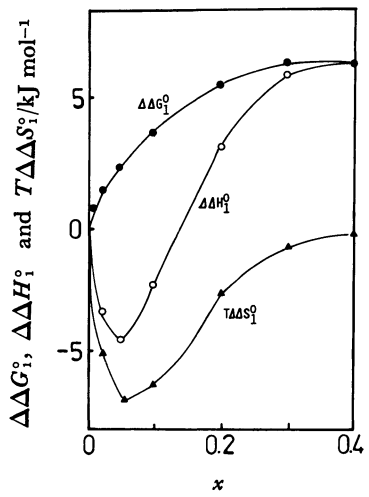

Fig. 4. Gibbs energies, enthalpies and entropies of formation of Hphen$^+$ in aqueous dioxane solutions relative to those in water.

By knowing values of $\Delta\Delta H_1^\circ$ and ΔH_t°(phen), the value of $\Delta H_t^\circ(\text{Hphen}^+) - \Delta H_t^\circ(\text{H}^+)$ was calculated according to Eq. 2, and the values of ΔH_1°, ΔH_t°(phen) and $\Delta H_t^\circ(\text{Hphen}^+) - \Delta H_t^\circ(\text{H}^+)$ thus calculated are summarized in Table 5. Since the enthalpy of transfer of proton $\Delta H_t^\circ(\text{H}^+)$ from water to the 0.2 mole fraction dioxane-water mixture was already reported in a previous paper,[9] $\Delta H_t^\circ(\text{Hphen}^+)$ from water to the mixture was also calculated and the values are also listed in Table 5.

Hphen$^+$ involves a hydrophilic $\gtrless$NH$^+$ group solvated with water and hydrophobic aromatic rings preferentially solvated with dioxane in aqueous dioxane solutions. The enthalpy of transfer of Hphen$^+$ from water to an aqueous dioxane solution should thus involve contributions of those of $\gtrless$NH$^+$ ($\Delta H_t^\circ(\gtrless\text{NH}^+)$) and aromatic rings ($\Delta H_t^\circ$(Ar)) within Hphen$^+$. The enthalpy of transfer of the $\gtrless$NH$^+$ group may be assumed to be similar to that of H$^+$, because it has been found that the enthalpy of transfer of the protonated ethylenediamine (Hen$^+$) from water to the 0.2 mole fraction dioxane-water mixture was very close to that of proton, *i.e.*, $\Delta H_t^\circ(\text{Hen}^+) \cong \Delta H_t^\circ(\text{H}^+)$.[9]

Table 5. Changes in enthalpy of formation of Hphen$^+$ relative to that in water and enthalpies of transfer ΔH_t°/kJ mol^{-1} of relevant species from water to aqueous dioxane solutions at 25 °C

x	$\Delta\Delta H_1^\circ$	ΔH_t°(phen)	$\Delta H_t^\circ(\text{Hphen}^+) - \Delta H_t^\circ(\text{H}^+)$	$\Delta H_t^\circ(\text{Hphen}^+)$	$\Delta H_t^\circ(\text{H}^+)$[a]
0.025	−3.1	4.5	1.4		
0.05	−4.1	6.3	2.2		
0.1	−2.1	8.7	6.6		
0.2	2.7	8.3	11.0	−11.7	−22.7
0.3	5.9	4.5	10.4		
0.4	6.4	5.4	11.8		

a) Ref. 9.

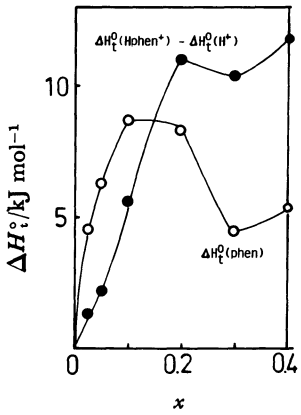

Fig. 5. Enthalpies of transfer, ΔH_t°(phen) and ΔH_t°(Hphen$^+$)$-\Delta H_t^\circ$(H$^+$), from water to aqueous dioxane solutions plotted against x.

If we assume that solvation of the protonated nitrogen atom $\gtrless$NH$^+$ within Hphen$^+$ with water varies in a similar manner to that of H$^+$ in the range x= 0—0.4, ΔH_t°(Hphen$^+$)$-\Delta H_t^\circ$(H$^+$) should approximately reflect the change in solvation of the aromatic rings within Hphen$^+$. Variations of ΔH_t°(Hphen$^+$)$-$ ΔH_t°(H$^+$) and ΔH_t°(phen) plotted against x (Fig. 5) show that they have a similar trend in the range x= 0—0.2. The result thus suggested that the aromatic rings within Hphen$^+$ was also significantly solvated with dioxane in the range of x up to 0.2. In the range x=0.2—0.3, ΔH_t°(phen) more steeply decreased with x than ΔH_t°(Hphen$^+$)$-\Delta H_t^\circ$(H$^+$), which may be caused by enhanced hydration at the sites of nitrogen atoms within 1,10-phenanthroline as discussed in a previous section.

The value ΔH_t°(Hphen$^+$) from water to the 0.2 mole fraction dioxane-water mixture was -11.7 kJ mol^{-1}, which should be represented as the sum of ΔH_t°($\gtrless$NH$^+$) and ΔH_t°(Ar). If we simply assume that ΔH_t°($\gtrless$NH$^+$)=ΔH_t° (H$^+$) in the range x=0—0.2, the value of ΔH_t°(Ar) from water to the 0.2 mole fraction dioxane-water mixture was estimated to be about 11 kJ mol^{-1}, which was slightly larger than ΔH_t°(phen) (8.3 kJ mol^{-1}). The slightly larger value of ΔH_t°(Ar) than ΔH_t°(phen) suggests that the hydration at the sites of nitrogen atoms within 1,10-phenanthroline was enhanced in the 0.2 mole fraction dioxane-water mixture relative to water.

Solvent Effects on the Formation of H(phen)$_2^+$. The formation of H(phen)$_2^+$ could be detected only in aqueous dioxane solutions of x<0.1, where the hydrogen-bonded structure of water in the bulk might still significantly remain and the stacks of 1,10-phenanthroline were expected to be formed.

Mitchell[14] suggested from measurements of the concentration dependence of the proton NMR spectrum of 1,10-phenanthroline in acidic solutions that considerable self-stacking occurred among 1,10-phenanthroline molecules to form the H(phen)$_2^+$ species. Considering that the H(phen)$_2^+$ species was not formed in aqueous dioxane solutions of relatively higher dioxane content in which the hydrogen-bonded structure of water in the bulk may be almost destructed, 1,10-phenanthroline molecules within H(phen)$_2^+$ may have a stacked structure. A suggested form for the structure of H(phen)$_2^+$ is illustrated in Fig. 6.

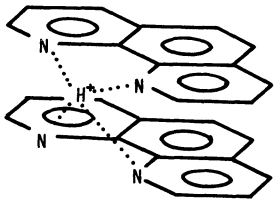

Fig. 6. The suggested structure of the H(phen)$_2^+$ species.

The values of ΔH_2° pertaining to the reaction, Hphen$^+$+phen=H(phen)$_2^+$, were negative in all aqueous dioxane solutions examined. The result can be expected because of negative enthalpies of formation of stacked oligomers of 1,10-phenanthroline (phen)$_n$.

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