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A Thermodynamic Study of the Synergistic Solvent Extraction of a Series of Zinc(II) and Cadmium(II) Complexes

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The extraction of zinc and cadmium using chloroform and benzene solutions constaining diphenylcarbazone (DPC=Hdpc), either alone or combined with pyridine(py) or 1,10-phenanthroline(phen), was studied thermodynamically. The formation constants were measured as functions of the temperature in order to ascertain the free energy, enthalpy, and entropy changes. The thermodynamic parameters support a proposed mechanism for the synergism of zinc in which the coordination number of the zinc ion expands with formation of $Zn(dpc)_2S$, where S is pyridine or 1,10-phenanthroline. On the other hand, the thermodynamic values for the synergistic reaction of cadmium support a mechanism in which pyridine or 1,10-phenanthroline replaces the residual waters of hydration in the first coordination sphere of cadmium.

In recent years, synergistic extractions have been studied by a number of workers. Considerable attention has been given to the mechanism of synergistic solvent extraction. Three possible mechanisms to explain the data of synergistic solvent extraction of metal ions by the combined action of two specific solutes in the organic phase have been proposed:[1]

(i) The neutral additive replaces the residual waters of hydration in the first coordination sphere of the metal ion.

(ii) The neutral additive attaches the metal chelate, by means of a hydrogen bond, to the coordinated waters of the first hydration sphere.

(iii) The coordination number of the non-hydrated chelate expands to accommodate the direct coordination of the adduct to the metal.

Knowledge of the formation constants alone does not allow one to choose between the three mechanisms proposed. However, if the enthalpies and entropies of the extraction reactions are known, it is possible to evaluate the mechanism of synergistic solvent extraction. Accordingly several studies of the thermodynamics of synergistic solvent extraction have been reported.[2-8] Kandil *et al.* have concluded that the mechanisms of adduct formation by tributylphosphate and acetylacetone with tris-thenoyltrifluoroacetone (TTA=Htta) chelates of Eu and Tm involve the expansion of the coordination number of the central metal ions from 6 to 8. These studies have also shown that the third mechanism fits the experimental data best.

Nakayama[9,10] has studied the effect of the temperature on the extraction of several metal chelates of 8-quinolinol. In a previous paper by the present authors it has been shown that the cadmium complex of diphenylcarbazone is quantitatively extracted in the presence of 1,10-phenanthroline and that an extract has a higher molar absorptivity than that for diphenylthiocarbazone (dithizone).[11] In this study, the temperature effects on the distribution equilibraia of zinc and cadmium chelates with DPC alone or when combined with pyridine or 1,10-phenanthroline have been examined in order to explain the extraction mechanism in terms of thermodynamic data.

Experimental

Reagents and Apparatus. The chemicals, such as cadmium, diphenylcarbazone, and 1,10-phenanthroline, used in the extraction have been previously described.[11]

A stock solution of zinc(II)[10^{-2} M(1 M=1 mol dm^{-3})] was prepared by dissolving weighed amounts of zinc chloride in dilute hydrochloric acid and then diluted with distilled water as required. The pyridine was purified by distillation under reduced pressure. All the other chemicals were of an analytical-reagent grade.

Extraction was carried out in a cylindrical tube with a magnetic stirrer in a constant-temperature bath.[9] The temperature was controlled to ± 0.1 °C by means of a thermoregulator. A Komatsu-Yamato Coolnics Dip (CTR-1, CTR-3B) was used for cooling. For the pH measurement, a Hitachi-Horiba M-5 pH meter equipped with a glass-calomel electrode pair for high-temperature work was used. All the other equipment used was the same as has previously been described.

Extraction Procedure. A 30 ml portion of a buffered cadmium or zinc solution was stirred with a 10 ml portion of the reagent solution in a cylindrical tube standing in a constant temperature bath for 30 min, a time period which was found adequate for the attainment of equilibrium. The ionic strength was adjusted by adding sodium sulfate at 0.05. Sodium perchlorate was not used because cadmium and zinc complexes of 1,10-phenanthroline were extracted into the organic phase by forming ion-pair complexes with sodium perchlorate.

After stirring, the pH value of the aqueous phase was measured *in situ*. After phase-separation, the aqueous phase was immediately analyzed with the atomic absorption spectrophotometer, whereas the organic phase was analyzed after back-extracting into an aqueous nitric acid solution.

Results and Discussion

Extraction of Zinc and Cadmium with DPC in the Absence of Phenanthroline and Pyridine. The behavior of the extraction of zinc and cadmium with DPC alone into chloroform and benzene was studied at various temperatures.

For Zn, the plots of log D *vs.* pH when chloroform was used are shown in Fig. 1. The slopes of log D *vs.* pH are 2 at each temperature. The plots of log D *vs.* log $[DPC]_0$ at a constant pH are linear, with a slope of

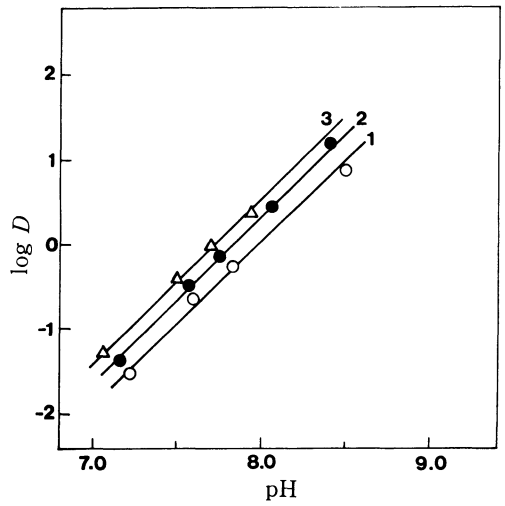

Fig. 1. Effect of pH on the distribution of zinc with DPC between chloroform and water.
$[DPC]_0 = 5 \times 10^{-4}$ M, $[Zn]_T = 10^{-5}$ M. 1: 25 °C, 2: 35 °C, 3: 45 °C.

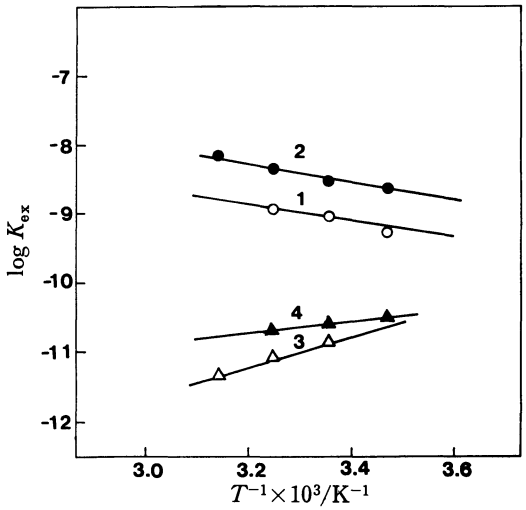

Fig. 2. Temperature effect on the distribution of zinc and cadmium between organic solvents and water.
1: Zinc into chloroform, 2: zinc into benzene, 3: cadmium into chloroform, 4: cadmium into benzene.

2. In the case of benzene, the slopes of log D *vs.* pH are 2 at each temperature, the same as those in chloroform. In this system, the slopes of log D *vs.* log $[DPC]_0$ at various temperatures are also 2. Thus, it can be concluded that only a single species, the simple 1 : 2 chelate, $Zn(dpc)_2$, is present in the organic phase. The overall reaction can be represented by Eq. 1:

$$Zn^{2+} + 2Hdpc_{(o)} \rightleftarrows Zn(dpc)_{2(o)} + 2H^+. \quad (1)$$

The extraction constant, K_{ex}, is a composite of the chelate formation constant, β_2, and its distribution constant, K_{DC}, as well as of the reagent acid-dissociation constant, K_a, and its distribution constant, K_{DR}:

$$K_{ex} = \beta_2 K_{DC} K_a^2 / K_{DR}^2. \quad (2)$$

The product, $\beta_2 K_{DC}$, corresponds to the heterogeneous equilibrium constant of the following reaction:

$$Zn^{2+} + 2dpc^- \overset{\beta_2 K_{DC}}{\rightleftarrows} Zn(dpc)_{2(o)}. \quad (3)$$

In the case of Cd, the plots of log D *vs.* pH in both solvents are linear and exhibit a slope of 2 at each temperature. The analogous log D *vs.* log $[DPC]_0$ plots are also linear, with a slope of 2. These results suggest that the extracted species of cadmium can also be expressed as a simple chelate, $Cd(dpc)_2$. Hence, the extraction constant of cadmium can be represented as:

$$K'_{ex} = \beta'_2 K'_{DC} K_a^2 / K_{DR}^2. \quad (4)$$

The plots of log K_{ex} *vs.* $1/T$ K are shown in Fig. 2. In the case of Zn, the distribution increases with an increase in the temperature. On the other hand, in the case of Cd, the distribution decreases with an increase in the temperature.

From these experimental data, the thermodynamic parameters, ΔG, ΔH, and ΔS, were calculated by using thermodynamic equations. These values are listed in Tables 1—3. The data in Table 1 show an endothermic

Table 1. Thermodynamic values for extraction of Zn^{2+} with dpc, dpc + phen, and dpc+py into chloroform and benzene at 25 °C

Species	log K_{ex}	ΔG kJ mol^{-1}	ΔH kJ mol^{-1}	ΔS J K^{-1} mol^{-1}
$Zn(dpc)_2$	−9.04	51.6	28.2	−79
$Zn(dpc)_2$·phen	−2.23	12.7	−28.1	−137
$Zn(dpc)_2$·py	−5.16	29.5	−18.3	−160
$Zn(dpc)_2$[a)]	−8.51	48.5	27.7	−70
	log β_{ad}[b)]			
$Zn(dpc)_2$·phen	6.81	−38.9	−56.3	−58
$Zn(dpc)_2$·py	3.88	−22.1	−46.5	−81

a) Into benzene. b) β_{ad} is the adduct-formation constant which corresponds to $K_{ex,ad}/K_{ex}$.

Table 2. Thermodynamic values for extraction of Cd^{2+} with dpc, dpc+phen, and dpc+py into chloroform at 25 °C

Species	log K_{ex}	ΔG kJ mol^{-1}	ΔH kJ mol^{-1}	ΔS J K^{-1} mol^{-1}
$Cd(dpc)_2$	−10.85	61.9	−42.6	−351
$Cd(dpc)_2$·phen	−3.05	17.4	−42.6	−201
$Cd(dpc)_2$·py	−7.29	41.6	−34.9	−257
	log β_{ad}			
$Cd(dpc)_2$·phen	7.80	−44.5	0.0	150
$Cd(dpc)_2$·py	3.56	−20.3	7.7	94

Table 3. Thermodynamic values for extraction of Cd^{2+} with dpc, dpc+phen, and dpc+py into benzene at 25 °C

Species	log K_{ex}	ΔG kJ mol^{-1}	ΔH kJ mol^{-1}	ΔS J K^{-1} mol^{-1}
$Cd(dpc)_2$	−10.61	60.5	−16.2	−257
$Cd(dpc)_2$·2phen	2.08	−11.9	−44.8	−111
$Cd(dpc)_2$·py	−7.04	40.2	−38.0	−262
	log β_{ad}			
$Cd(dpc)_2$2phen	12.69	−72.4	−28.6	146
$Cd(dpc)_2$py	3.57	−20.3	−21.8	−5

TABLE 4. $\Delta(\Delta H)(=\Delta H_{Zn}-\Delta H_{Cd})$ AND $\Delta(\Delta S)$ $(=\Delta S_{Zn}-\Delta S_{Cd})$ VALUES FOR EXTRACTION BETWEEN WATER AND ORGANIC SOLVENTS

Solvents	$\Delta(H)$ / kJ mol^{-1}	$\Delta(\Delta S)$ / J K^{-1} mol^{-1}
Chloroform	70.8	272
Benzene	43.9	187

reaction for the formation of the Zn–DPC chelate. It has been reported that this behavior is quite characteristic of chelation reactions in which the waters of the inner-coordination sphere of the metal ion are displaced by the chelating reagent.[12] The extraction constants of the two metal chelates can be represented as Eqs. 3 and 4, but K_a and K_{DR} are independent of the metal. Therefore, by using the same solvent, the difference in the extraction constant between the two metal chelates can be related to the difference in the product, $\beta_2 K_{DC}$ $(\beta'_2 K'_{DC})$. Hence, $\Delta(\Delta H)$, which is the difference in enthalpy change calculated from the values of the extraction constant, can be represented as the sum of the difference in the enthalpy change of the chelate formation and of the distribution between the metal chelates. The calculated values of $\Delta(\Delta H)$ and $\Delta(\Delta S)$ are listed in Table 4. The values of $\Delta(\Delta H)$ are largely positive. If the extracted species of Zn had a composition like that of Cd, $\Delta(\Delta H)$ would be predicted to be fairly small, for the difference in enthalpy change of the chelate formation between Zn and Cd is generally small. Hence, it is conceivable that the extracted species of Zn is different from that of Cd. As for lanthanoids, ΔH, which is calculated from the extraction constant, has been reported to be 11.1 kcal/mol (46.4 kJ mol^{-1}) for $Eu(tta)_3$, 9.64 kcal/mol (40.3 kJ mol^{-1}) for $Tb(tta)_3$, and 12.4 kcal/mol (51.9 kJ mol^{-1}) for $Tm(tta)_3$.[3,5] The difference between the ΔH values of these lanthanoids is very small. The positive values of $\Delta(\Delta H)$ and $\Delta(\Delta S)$ would indicate that water molecules would be removed from Zn–DPC chelate in the process of extraction. Since hydrogen-bond energies are usually in the range of 10—25 kJ mol^{-1}, it would be expected to take ΔH values of 20—50 kJ mol^{-1} in order to remove two water molecules. The values of $\Delta(\Delta H)$ are 70.8 kJ mol^{-1} in the case of chloroform and 43.9 kJ mol^{-1} in the case of benzene. Therefore, these values are consistent with the postulate that the Zn–DPC chelate would be extracted as a non-hydrated chelate, $Zn(dpc)_2$, while the Cd–DPC chelate would be extracted as a hydrated species, $Cd(dpc)_2 \cdot 2H_2O$.

Furthermore, it became apparent from these results that the separation of zinc and cadmium may be further enhanced at high temperatures. For the purpose of enhancing the separation of zinc and cadmium, chloroform is better than benzene as the solvent for extraction. However, since chloroform has a low boiling point, for this purpose organic solvents whose boiling points are relatively high, such as 1,1,2,2-tetrachloroethane (TCE), are desirable. It was indicated that the separation of zinc and cadmium is further enhanced at high temperatures when both metals are extracted with 2-methyl-8-quinolinol into TCE.[13] Hence, it is conceivable that

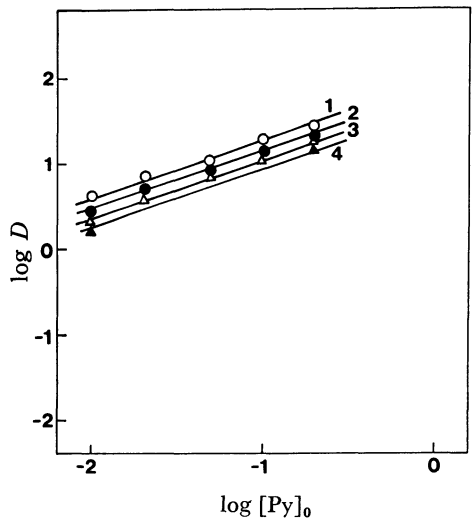

Fig. 3. Distribution of zinc with mixtures of DPC and pyridine into chloroform as a function of the pyridine concentration.
$[DPC]_0 = 5 \times 10^{-4}$ M, $[Zn]_T = 10^{-5}$ M, pH 7.0. 1: 15 °C, 2: 25 °C, 3: 35 °C, 4: 45 °C.

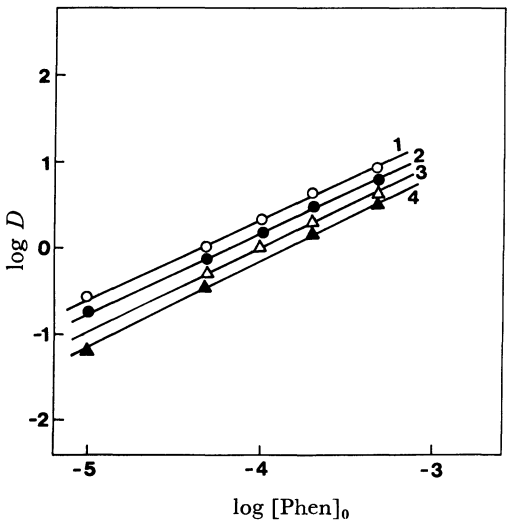

Fig. 4. Distribution of zinc with mixture of DPC and phenanthroline into chloroform as a function of the phenanthroline concentration.
$[DPC]_0 = 5 \times 10^{-4}$ M, $[Zn]_T = 10^{-5}$ M, pH 6.5. 1: 15 °C, 2: 25 °C, 3: 35 °C, 4: 45 °C.

solvent extraction at high temperatures may be applied to the separation of metals of the same group by using the difference in extraction mechanism between those metals.

Extraction of Zinc with DPC in the Presence of 1,10-*Phenanthroline or Pyridine.* By slope analysis, the extraction of Zn with DPC into chloroform in the presence of 1,10-phenanthroline or pyridine was studied at various temperatures. The log D *vs.* pH plots are linear and exhibit a slope of 2 at each temperature. The plots of log D *vs.* log $[py]_0$ are shown in Fig. 3. The slopes of log D *vs.* log $[py]_0$ are unity, irrespective of the temperature. In Fig. 4, the plots of log D *vs.* log $[phen]_0$ are shown. The slopes of log D *vs.* log

$[phen]_0$ are also unity, irrespective of the temperature. These results indicate that the extracted species are $Zn(dpc)_2 \cdot py$ and $Zn(dpc)_2 \cdot phen$ respectively. These thermodynamic parameters are summarized in Table 1.

In the presence of pyridine, the value of ΔG, which is calculated from the adduct-formation constant, is negative, so it is obvious that the acceptor mother chelate is stabilized by the adduct-chelate formation. The rather large negative experimental enthalpy ($\Delta H = -46.5$ kJ mol^{-1}) clearly eliminates Mechanism (i), because in this system the enthalpy change would be small, since the number of bonds to zinc does not change. Furthermore, in the case of Mechanism (ii), the enthalpy change would be the energy of the hydrogen bond ($\approx$10 to 25 kJ mol^{-1}). Therefore, it may be concluded that the mechanism most likely to explain the experimental results is Mechanism (iii), in which the coordination number of zinc expands from four to five to accommodate the neutral pyridine molecule.

Hence, the synergistic reaction in the organic phase can be expressed as follows:

$$Zn(dpc)_{2(o)} + py_{(o)} \rightleftarrows Zn(dpc)_2 \cdot py_{(o)}. \quad (5)$$

In this case, the entropy change would be largely negative, consisting of the cratic part ($\Delta n = -1$), where Δn is the change in the number of species, and the unitary part of pyridine. The rather large negative experimental entropy change ($\Delta S = -81$ J K^{-1} mol^{-1}) fits Eq. 5. The experimental results for 1,10-phenanthroline are $\Delta H = -56.3$ kJ mol^{-1} and $\Delta S = -58$ J K^{-1} mol^{-1}, which fit only Mechanism (iii).

The synergistic reaction in the organic phase can be represented by Eq. 6:

$$Zn(dpc)_{2(o)} + phen_{(o)} \rightleftarrows Zn(dpc)_2 \cdot phen_{(o)}. \quad (6)$$

Since 1,10-phenanthroline is usually bidentate, in this case the coordination number of zinc increases from four to six. Compared with pyridine, both entropy and enthalpy favor adduct-chelate formation.

Extraction of Cadmium with DPC in the Presence of 1,10-Phenanthroline or Pyridine. The extraction of cadmium with DPC into chloroform and benzene in the presence of 1,10-phenanthroline or pyridine was studied at various temperatures.

In the case of chloroform, the slopes of log D *vs.* pH are 2 at each temperature in the presence of both pyridine and 1,10-phenanthroline, and the distribution ratio decreased with an increase in the temperature. The slopes of log D *vs.* log $[DPC]_0$ are also 2 at each temperature. In the presence of pyridine, the slopes of log D *vs.* log $[py]_0$ are unity. In the presence of 1,10-phenanthroline, the slopes of log D *vs.* log $[phen]_0$ are also unity. These results suggest that the extracted species are $Cd(dpc)_2 \cdot py$ and $Cd(dpc)_2 \cdot phen$. From these results, the thermodynamic parameters, ΔG, ΔH, and ΔS, which were calculated from the thermodynamic equations, are as listed in Table 2. The values of ΔG, which were calculated from the adduct-formation constant, are negative, so it is obvious that the acceptor mother chelates are stabilized by the adduct-chelate formation. In these cases, the ΔH values, which are 7.7 kJ mol^{-1} for pyridine and 0.0 kJ mol^{-1} for 1,10-phenanthroline, are quite small, or even close to zero.

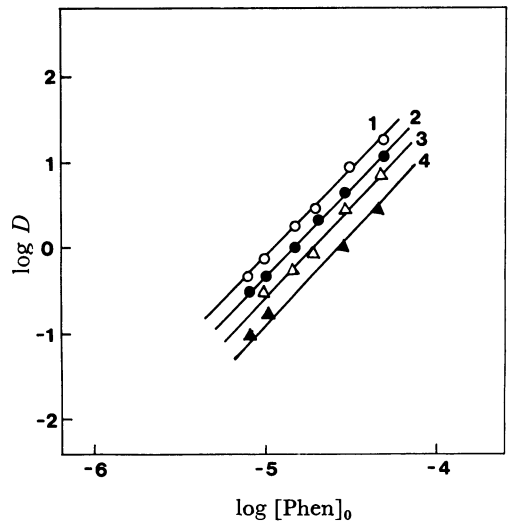

Fig. 5. Distribution of cadmium with mixtures of DPC and phenanthroline into benzene as a function of the phenanthroline concentration.
$[DPC]_0 = 5 \times 10^{-4}$ M, $[Cd]_T = 10^{-6}$ M, pH 7.1. 1: 15 °C, 2: 25 °C, 3: 35 °C, 4: 45 °C.

These relatively small experimental enthalpy changes clearly eliminate Mechanism (iii). These results fit the postulate that, in the absence of pyridine or 1,10-phenanthroline, the Cd–DPC chelate would be extracted as a hydrated species, $Cd(dpc)_2 \cdot 2H_2O$. In the case of Mechanism (ii), the entropy change would be largely negative, since Δn, the change in the number of species, decreases. However, the experimental entropy changes are positive, so these results do no fit Mechanism (ii). Consequently, we may conclude that the mechanism (ii). Consequently, we may conclude that the mechanism most likely to explain the experimental results is Mechanism (i), in which pyridine or 1,10-phenanthroline replaces the residual waters of hydration in the first coordination sphere of the cadmium ion.

Hence, the synergistic reaction in the organic phase can be expressed as follows:

$$Cd(dpc)_2 \cdot 2H_2O_{(o)} + S_{(o)} \rightleftarrows Cd(dpc)_2 S_{(o)} + 2H_2O, \quad (7)$$

where S is pyridine or 1,10-phenanthroline.

Next, in the case of benzene, the slopes of log D *vs.* pH are 2 at each temperature in the presence of pyridine or 1,10-phenanthroline, and the distribution ratio decreases with an increase in the temperature. The slopes of log D *vs.* log $[DPC]_0$ are also 2. In the presence of pyridine, the slopes of log D *vs.* log $[py]_0$ are unity. In the presence of 1,10-phenanthroline, the plots of log D *vs.* log $[phen]_0$ are as shown in Fig. 5. The slopes of log D *vs.* log $[phen]_0$ are 2 at each temperature, unlike those with chloroform. These results suggest the idea that the extracted species are $Cd(dpc)_2 \cdot py$ and $Cd(dpc)_2 \cdot 2phen$. The thermodynamic parameters led to from these results are summarized in Table 3. The values of ΔG are largely negative, so the acceptor mother chelates are obviously stabilized by the adduct-chelate formation. In the absence of pyridine or 1,10-phenanthroline, the Cd–DPC chelate would be extracted into benzene as a hydrated species, $Cd(dpc)_2 \cdot 2H_2O$,

like that into chloroform, so it may be concluded that the mechanism most likely to explain the experimental results is Mechanism (i), in which pyridine or 1,10-phenanthroline replaces the residual waters of hydration in the first coordination sphere of the cadmium ion. Compared with the case of pyridine, in the case of 1,10-phenanthroline both entropy and enthalpy changes favor adduct-chelate formation : however, the contribution of the entropy change is larger than that of enthalpy. The difference in ΔS between pyridine and 1,10-phenanthroline in benzene is larger than that in chloroform. A large entropy change of this order reflects the steric hindrance caused by the first 1,10-phenanthroline molecule to the entrance of its second molecule. Furthermore, the steric effect may make it difficult for 1,10-phenanthroline to form a strong bond with the complex.

Thus, the thermodynamic results suggest that the mechanism for the synergism of zinc is different from that of cadmium.

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