Table II. Representative Data for the Production of $Na_2S_2O_4$ in 0.1 M SO_2/0.5 M [*n*-Bu_4N]ClO_4/CH_3CN Solutions

electrode[a] (area, cm²)	potential vs. Ag/Ag^+,[b] V	current dens, mA/cm²[c]	*t*, h[d]	charge passed, C	$Na_2S_2O_4$ collected, mg[e]	η_i, %[f]
Pt (0.07)	−1.0	9.0	50	110	95	95
p-WS_2 (0.07)	−0.8	4.2	30	32	27	93
textured p-Si (0.07)	−0.8	6.0	80	120	104	96
textured p-Si (1.0)	−0.8	13.5	3	146	125	95
platinized p-InP (0.03)	−0.4	6.7	60	43	36	92

[a] Photocathodes were irradiated with ~40 mW/cm² of 632.8-nm light provided by a He-Ne laser except for the 1.0 cm² textured p-Si electrode, where an incandescent lamp providing >100 mW/cm² was employed. [b] Potential held in the cathode compartment of a two-compartment cell containing 100.0 mL of 0.1 M SO_2 in 0.5 M [*n*-Bu_4N]ClO_4/CH_3CN. [c] The measured photocurrent was constant, ±5%, in all experiments. [d] Time of cell operation. [e] Weight of the solid obtained upon addition of excess $NaClO_4$ to the catholyte. These amounts of $Na_2S_2O_4$ represent consumption of less than 10% of the total SO_2 originally present in the catholyte. [f] Current efficiency for $Na_2S_2O_4$ production with the assumption that the solid collected is 100% $Na_2S_2O_4$.

in 0.5 M [*n*-Bu_4N]ClO_4/CH_3CN results in a current density that is stable to within 5%. Upon completion of the electrolysis, addition of excess $NaClO_4$ caused formation of a fine, white precipitate, which is assayed to be >95% $Na_2S_2O_4$ by titration with methylene blue solution. The quantities of $Na_2S_2O_4$ collected represent consumption of less than 10% of the SO_2 originally present in the catholyte, consistent with little or no variation in current density. Further verification that the powders are indeed $Na_2S_2O_4$ is obtained by noting the similarity of IR absorptions (400–4000 cm^{-1}) of the electrolysis samples and commercially available $Na_2S_2O_4$, although impurities in both prevent an exact spectral match.

Conclusions

Our data establish that illuminated p-type Si, WS_2, and InP electrodes can be used to lower the electrical energy requirement in the electrochemical generation of $Na_2S_2O_4$ from SO_2/CH_3CN/0.5 M [*n*-Bu_4N]ClO_4 solutions. Since $E°'(SO_2/S_2O_4^{2-})$ in this medium is difficult to obtain, we must compare the photoelectrodes to an electrode, Pt, which is presumed to have rapid interfacial kinetics. Such a comparison is meaningful, since it gives a guide to the actual reduction in the electrical energy requirement for operation of a photoelectrosynthetic cell[1] compared to that for a conventional electrolytic cell. In any case, it is clear that platinized p-InP is the material of choice, as the power savings efficiency for conversion of 514.5-nm light is up to 11%. The durability of all of the photocathodes, particularly the platinized p-type InP, is good, and indeed the generation of synthetically significant quantities of $Na_2S_2O_4$ can be effected with >90% current efficiency. Others[6b] have shown that η_{max} exceeds 12% *solar efficiency* for the generation of H_2 from platinized p-InP. This suggests that the solar efficiency for $S_2O_4^{2-}$ production could be practically significant. However, the use of single-crystal InP electrode materials would likely be prohibitively expensive for practical applications.

Acknowledgment. We thank the United States Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, for support of this research.

Registry No. SO_2, 7446-09-5; Si, 7440-21-3; WS_2, 12138-09-9; InP, 22398-80-7; Pt, 7440-06-4; $Na_2S_2O_4$, 7775-14-6.

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Studies of Formation of Zinc(II) Bromide, Iodide, and Thiocyanate Complexes in Methanol Using the Respective Ion-Selective Electrodes

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The formation of ZnX_n^{2-n} (X^- stands for Br^-, I^-, and NCS^-, respectively) complexes in methanol has been studied by X^- ion measurements with Ag–AgX electrodes. All measurements have been made at an ionic strength of 0.05 M, adjusted with sodium and zinc perchlorates, and in a closed cell thermostated at 25.0 ± 0.1 °C. In the complexation of zinc(II) chloride in methanol, the cooperative phenomenon that the stepwise stability constant of a monochloride complex is smaller than that of a dichloride complex has already been reported. In the present studies, this same phenomenon has been also observed in the formation of bromide and iodide complexes of zinc(II). The degree of cooperativity steadily increases in going from the chloride to the iodide complex of zinc(II). On the other hand, the magnitude of stepwise stability constants of zinc(II) thiocyanate complexes is in the order generally found; that is, the constants decrease in going from the mono- to the tetrathiocyanate complex.

Introduction

Since many investigations of the equilibria of metal complexes have been made in aqueous solutions because of their great practical value, it is necessary to conduct these research studies in nonaqueous solvents so that one may understand the equilibrium constants theoretically and consistently. Generally, the stepwise stability constants of metal complexes, K_n, decrease with the increasing numerical value of n.[1] There are, however, some complexes that disobey the general trend for K_n values, and some of them have been already reported elsewhere.[2,3] Then, as shown in some literature references,[4] zinc(II) halide complexes are typical of the cooperative phenomenon. In order to gain further insight into this phenomenon, we have studied the stabilities of ZnX_n^{2-n} complexes (X^- stands for Br^-, I^-, and NCS^-, respectively) in methanol. Ex-

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(1) King, E. L. *Inorg. Chem.* **1981**, *20*, 2350–2352.

(2) Doe, H.; Kitagawa, T. *Inorg. Chem.* **1982**, *21*, 2272–2276.

(3) Doe, H.; Matsui, M.; Shigematsu, T. *Bull. Inst. Chem. Res., Kyoto Univ.* **1980**, *58* (2), 154–163.

(4) (a) Ahrland, S.; Björk, N.-O. *Acta Chem. Scand., Ser. A* **1976**, *A30*, 256–269. (b) Ahrland, S.; Björk, N.-O.; Portanova, R. *Ibid.* **1976**, *A30*, 270–276. (c) Hoffman, H. *Pure Appl. Chem.* **1975**, *41*, 327–354. (d) Libuš, W.; Pastewski, R.; Sadowska, T. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 377–387.

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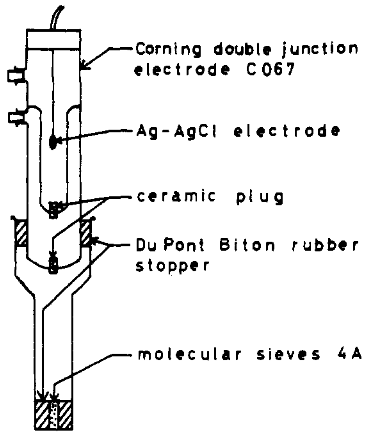

Figure 1. Sketch of the reference electrode.

periments have been carried out by potentiometry with X^- ion-selective electrodes, which is a very reliable technique for the measurement of ionic equilibria in solutions. All measurements have been conducted at a relatively low ionic strength of 0.05 M in order to estimate the thermodynamic constants by using the Debye–Hückel theory of ion activity.

Experimental Section

Materials. Both sodium bromide and iodide (special grade, Wako) were dried at 110 °C for 2 h,[5] and they were used to prepare their respective 0.1 M methanolic stock solutions. The preparations of other reagents were described in a previous paper.[2]

Instrumentation. The outline of instrumentation was described previously.[2] The Ag–AgBr electrode was made by coating silver and silver bromide on a platinum wire electrolytically. The sensors for I^- and NCS^- ions were National IE-50105 iodide-selective and Corning A006CNS thiocyanate-selective electrodes, respectively.

In this work, the reference electrode was improved. The new reference electrode had a triple junction as shown in Figure 1. The internal chamber of the electrode was filled with an aqueous solution of 1.0 M NaCl saturated with AgCl and the middle portion with 0.10 M $NaClO_4$ aqueous solution. The external reservoir connected to the smaple solution by the plug of 4A molecular sieves contained 0.10 M $NaClO_4$ in methanol. This ceramic-plug bridge excellently isolated the sample solution from the interior solutions, and this electrode stabilized the electromotive force, emf, of the cell. If the temperature of the reference electrode placed outside a thermostated cell was also maintained constant throughout the experiment, drifts of the emf were not observed for sequential measurements, and reproducibility of measurements was well within ±0.5 mV from day to day. Although it took 1 h for the initial emf in sequential measurements to reach equilibrium, the following emf values reached equilibrium generally within 5 min.

All measurements were carried out in closed cells, thermostated at 25.0 ± 0.1 °C by a Tokyo Rikakikai Type UC-65 Uni Cool. Solutions of 50-cm³ amounts containing known amounts of $Zn(ClO_4)_2$ and $NaClO_4$ were titrated with several successive portions of the same solution containing additional known amounts of NaX. After the last NaX addition, the emf of the standard solution of NaX not containing $Zn(ClO_4)_2$ was recorded. The standard and sample solutions had the same ionic strength of 0.050 M. More detailed procedures are described elsewhere.[2] The calibration curves of each anion, X^-, were always linear with the slope of the Nernst relationship, 59.1 mV/decade, in the concentration range of our measurements.

Data Treatment and Results

A more complete discussion of our theory can be found in ref 2. We consider the equilibria

$$ZnX_{n-1}^{3-n} + X^- \rightleftarrows ZnX_n^{2-n} \quad (K_n) \tag{1}$$

$$Zn^{2+} + ClO_4^- \rightleftarrows ZnClO_4^+ \quad (K_{1A}) \tag{2}$$

$$ZnX^+ + ClO_4^- \rightleftarrows ZnX{\cdot}ClO_4 \quad (K_{mA}) \tag{3}$$

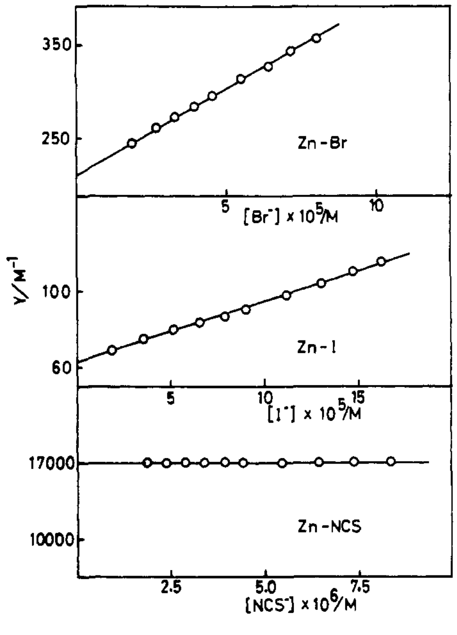

Figure 2. Y vs. $[X^-]$ plots according to eq 4. For the Zn–Br system, $C^\circ_{Zn} = 1.51_6 \times 10^{-2}$ M and $C^\circ_I = 1.00 \times 10^{-2}$ M; for the Zn–I system, $C^\circ_{Zn} = 1.33_3 \times 10^{-2}$ M and $C^\circ_I = 1.50 \times 10^{-2}$ M; for the Zn–NCS system, $C^\circ_{Zn} = 1.14_8 \times 10^{-2}$ M and $C^\circ_I = 2.00 \times 10^{-2}$ M.

The concentration of X^- is relatively low in these solutions; hence, the concentrations of ZnX_3^- and ZnX_4^{2-} are negligible, yielding under some assumption

$$Y = \Delta_X/([Zn^{2+}][X^-]) = y_{2+}K_1(1 + y_\pm^2 K_{mA}[ClO_4^-]) + 2y_{2+}y_\pm^2 K_1 K_2[X^-] \tag{4}$$

where

$$\Delta_X = C^\circ_X - [X^-]$$

C°_X is the initial concentration of NaX, and y_{2+} and $y_\pm$ are the ion activity coefficients of Zn^{2+} and ClO_4^- ions, respectively. The concentrations of Zn^{2+} and ClO_4^- ions in eq 4 can be calculated by the equations

$$y_{2+}K_{1A}[Zn^{2+}]^2 + \{y_{2+}K_{1A}(C^\circ_I + C^\circ_{Zn} + \Delta_X) + 1\}[Zn^{2+}] - (C^\circ_{Zn} - \Delta_X) = 0 \tag{5}$$

$$[ClO_4^-] = C^\circ_I + C^\circ_{Zn} + [Zn^{2+}] + \Delta_X \tag{6}$$

where C°_I and C°_{Zn} are the initial concentrations of $NaClO_4$ and $Zn(ClO_4)_2$, respectively. The values of y_{2+} and $y_\pm$ are calculated by the Debye–Hückel second approximation with values of 6 and 4 Å for the ion size parameters, a, respectively. At an ionic strength of 0.05 M, y_{2+} and $y_\pm$ are 0.0976 and 0.510, respectively. The value of K_{1A} for zinc perchlorate is 60.4 M^{-1}.[2]

The range of C°_X of $(5 \times 10^{-5}) - (4.5 \times 10^{-4})$ M was used for Br^- and I^- and $(3 \times 10^{-4}) - (1.9 \times 10^{-3})$ M for NCS^-. A set of sequential measurements was made at a constant concentration of ClO_4^- ion. For each system of Zn^{2+}–X^-, several sets of measurements that have values of C°_{Zn} different from each other were carried out at a constant ionic strength. C°_{Zn} and C°_I used for the ionic strength of 0.05 M were the same as those used in ref 2. The method of determining those values to achieve a constant ionic strength medium can be also found in the paper. The results calculated by eq 4–6 are summarized in Table I.

Figure 2 shows a graphic representation of each system. As revealed in Table I and Figure 2, the K_2 value of the zinc thiocyanate system is very small as compared with the K_1 value. Therefore, since we could not obtain the K_2 value

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(5) "Shin Jikken Kagaku Koza"; Maruzen: Tokyo, 1976; Vol. 8, Chapters 1–3.

Table I. Results of Calculations Based on Eq 4 for Zinc Bromide, Iodide, and Thiocyanate Systems at 25.0 °C and $I = 5.0 \times 10^{-2}$ M

$10^2C°_{Zn}$/ M	$10^2C°_I$/ M	$10^2[ClO_4^-]$/ M	$10^{-6}2y_{2+}y_{\pm}^2K_1K_2$/ M^{-2}	$y_{2+}K_1 \times (1 + y_{\pm}^2K_{mA}[ClO_4^-])$/ M^{-1}	r
			1. Zinc Bromide		
1.87_7	0.00	3.44_0	1.62_8	$217._2$	0.9997
1.69_8	0.50	3.60_2	1.66_2	$212._6$	0.9987
1.51_6	1.00	3.76_0	1.76_2	$213._9$	0.9999
1.33_3	1.50	3.91_9	1.61_4	$214._6$	0.9983
1.14_8	2.00	4.07_7	1.77_5	$218._4$	0.9993
0.96_1	2.50	4.23_3	1.63_2	$228._3$	0.9994
			2. Zinc Iodide		
1.87_7	0.00	3.44_0	0.343_9	64.3_3	0.9988
1.69_8	0.50	3.60_1	0.345_0	60.6_4	0.9939
1.51_6	1.00	3.76_2	0.319_0	62.3_5	0.9985
1.33_3	1.50	3.91_8	0.321_0	61.7_5	0.9985
0.96_1	2.50	4.23_1	0.317_8	65.2_3	0.9951
			3. Zinc Thiocyanate		
1.87_7	0.00	3.45_4	-9.3_4	$1.67_3 \times 10^4$	0.4095
1.51_6	1.00	3.77_5	-5.0_1	$1.73_8 \times 10^4$	0.5024
1.33_3	1.50	3.93_5	-7.1_3	$1.69_5 \times 10^4$	0.3132
1.14_8	2.00	4.09_3	16.7_9	$1.69_5 \times 10^4$	0.5758
1.14_8	2.00	4.09_3	24.2_9	$1.69_0 \times 10^4$	0.9263

Table II. Concentration Stability Constants of Zn(II)–X⁻ Systems in Methanol at 25.0 °C and $I = 5.0 \times 10^{-2}$ M

syst	y_1K_1/M^{-1}	y_2K_2/M^{-1}	y_3K_3/M^{-1}	y_4K_4/M^{-1}
Zn-Cl[a]	$(7.57 \pm 0.17) \times 10^2$	$(4.52 \pm 0.27) \times 10^3$	4.0×10^2	7.0×10
Zn-Br	$(2.18 \pm 0.06) \times 10^2$	$(3.86 \pm 0.13) \times 10^3$		
Zn-I	$(6.29 \pm 0.19) \times 10$	$(2.62 \pm 0.11) \times 10^3$		
Zn-NCS	$(1.70 \pm 0.02) \times 10^4$	$(1.15 \pm 4.54) \times 10^2$ 1.02×10^3 [b]	1.04×10^3 [b]	3.50×10^2 [b]

[a] Reference 2. [b] Results of calculations based on eq 7.

Table III. Thermodynamic Stability Constants of Zn(II)–X⁻ Systems in Methanol at 25.0 °C

syst	K_1/M^{-1}	K_2/M^{-1}	K_3/M^{-1}	K_4/M^{-1}
Zn-Cl[a]	$(7.76 \pm 0.18) \times 10^3$	$(1.74 \pm 0.10) \times 10^4$	4.0×10^2	2.6×10
Zn-Br	$(2.23 \pm 0.06) \times 10^3$	$(1.48 \pm 0.05) \times 10^4$		
Zn-I	$(6.44 \pm 0.19) \times 10^2$	$(1.01 \pm 0.04) \times 10^4$		
Zn-NCS	$(1.74 \pm 0.03) \times 10^5$	3.92×10^3 [b]	1.04×10^3 [b]	1.30×10^2 [b]

[a] Reference 2. [b] Results of calculations based on eq 7.

accurately with the treatment of eq 4, simultaneously with the K_3 and K_4 values, it was estimated by the general Bjerrum $\bar{n}$ function (eq 7). In this equation, the term that includes K_{mA}

$$\bar{n} = \Delta_X/C°_{Zn} = \sum_{n=1}^{4} n\left(\prod_{i=1}^{n} y_iK_i\right)[X^-]^n / \left\{(1 + y_{2+}K_{1A}[ClO_4^-]) + \sum_{n=1}^{4}\left(\prod_{i=1}^{n} y_iK_i\right)[X^-]^n\right\} \quad (7)$$

is neglected. The plot of $\bar{n}$ values vs. log [X⁻] for the zinc thiocyanate system is indicated in Figure 3. This plot is compared with the plot for the zinc chloride system.

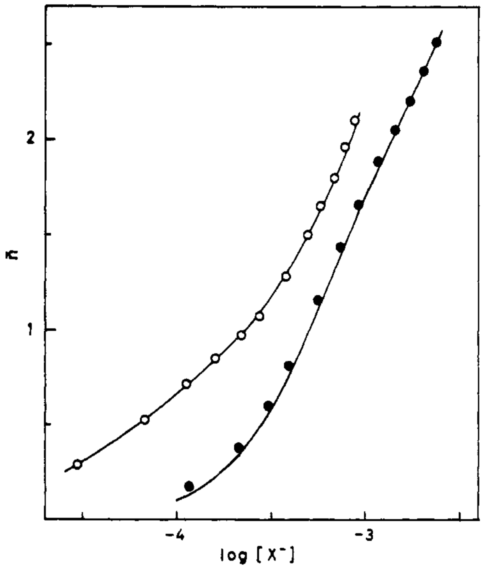

Figure 3. Average coordination numbers, $\bar{n}$, as a function of log [X⁻]: (●) zinc chloride, $C°_{Zn} = 2.73_2 \times 10^{-4}$ M, $C°_I = 5.00 \times 10^{-2}$ M; (○) zinc thiocyanate, $C°_{Zn} = 1.78_8 \times 10^{-4}$ M, $C°_I = 5.00 \times 10^{-2}$ M.

The concentration stability constants that are calculated from eq 4 and 7 are summarized in Table II in comparison with those of the zinc chloride system. In order to obtain thermodynamic values, we attempted the following. If the ion activity coefficients of ions of identical charge are equal, the ion activity coefficients, y_n, in Table II are related to y_{2+} and $y_{\pm}$ as follows: $y_1 = y_{2+}$, $y_2 = y_{\pm}^2$, $y_3 = 1$, $y_4 = y_{\pm}^2/y_{2+}$. Though ions like X⁻, ZnX⁺, and ZnX_3^- have different charge distributions and probably also different solvation forms, these effects for ion activity will be very small at a low ionic strength. Therefore, when experiments are made in low ionic strength media, this bold assumption for the ion activity coefficients is probably acceptable, and the use of the Debye–Hückel second approximation is also suitable for calculating them. We think our media of $I = 0.05$ M are in a permissible range for this purpose. Thus, using the above relations and the Debye–Hückel equation, we calcualted the thermodynamic stability constants in Table III from the results in Table II. The errors in the tables were computed from the standard deviation of intercepts and slopes in Table I according to the propagation rule of errors.

Discussion

In previous papers,[2,3] we have discussed whether or not the $y_{\pm}^2K_{mA}[ClO_4^-]$ term in eq 4 is negligible, e.g., whether or not the amount of $ZnX{\cdot}ClO_4$ is very small compared with that of ZnX^- in our systems. In this work, it has been also confirmed by changing ClO_4^- concentrations that the $y_{\pm}^2K_{mA}[ClO_4^-]$ values are negligibly small. As shown in the representation of the intercept, $y_{2+}K_1(1 + y_{\pm}^2K_{mA}[ClO_4^-])$, it is clear that there is a linear relationship between the intercept and the ClO_4^- concentration. However, one can only find similar figures with no relation in the fifth column of Table I, the values of intercept, for each system, though the ClO_4^- concentration varies. This means that $y_{\pm}^2K_{mA}[ClO_4^-] << 1$ and that the intercept is nearly equal to $y_{2+}K_1$. Thus, the K_{mA} is very small and the existence of $ZnX{\cdot}ClO_4$ is negligible in our systems.

The results in Table I also indicate that our theory for these systems is very reliable, partly because the values of the correlation coefficients, *r*, are nearly equal to 1; that is, these plots according to eq 4 give good straight lines (see Figure 2) partly because the slopes are also in good agreement with each other for each system as are the intercepts, in spite of the results at different C°_{Zn} and C°_I. The results employed for the latter case also involve an important suggestion that the media used, which differ somewhat in composition, have the same ionic strength. That is to say, this indicates that our attempt to achieve media with a constant ionic strength by the adjustment of C°_{Zn} and C°_I is satisfactorily carried out probably because of the low ionic strength.

For the zinc thiocyanate system, for which it was difficult to obtain the K_2 value from the treatment based on eq 4, we used Bjerrum's $\bar{n}$ function (eq 7) to determine the K_2, K_3, and K_4 values. However, the treatment of eq 7 was not applied to the estimation of K_3 and K_4 of the zinc bromide and iodide systems because these values were too small to be estimated accurately at the low ionic strength of 0.05 M. As can be seen in Figure 3, it is clear that the zinc chloride system involves a steeper increase in the $\bar{n}$ value with log $[X^-]$ than the zinc thiocyanate system. That is to say, the zinc chloride system is typical of cooperativity and the thiocyanate is typical of anticooperativity.[1] The figure involves curves calculated with the stability constants which are adjusted to obtain the best fit between observed and calculated values.

The concentration stability constants with $I = 0.05$ M are summarized in Table II. In the table, the values obtained by the treatment based on eq 7 are shown together with the values obtained from eq 4. The values calculated by eq 7 are indicated without estimates of the errors. For all the zinc halide systems $y_1K_1 < y_2K_2$. On the other hand, however, $y_1K_1 > y_2K_2$ for the zinc thiocyanate system, and this is generally true. The y_2K_2 value for the zinc thiocyanate system from eq 4 contains a large error because the correlation coefficients in Table I have small values, that is, because the slopes in eq 4 are very gentle as shown in Figure 2. Therefore, we are sure that the y_2K_2 value from eq 7 is more reliable than that from eq 4.

It is known that thermodynamic constants are necessary to discuss equilibria theoretically. Our assumptions for ion activity make the sequence of the thermodynamic stability constant, K_n, the same as that of the concentration constant, y_nK_n, and the discussion of the trend in K_n for the various ligands is based equally on consideration of y_nK_n, though one can sometimes find small differences in the sequence of stability constants with the various *n* values for a given ligand between y_nK_n and K_n. However, we think it is significant to estimate the thermodynamic values if possible. On the basis of the idea and method in Data Treatment and Results, we have computed the stepwise thermodynamic stability constants in Table III. Figure 4 is a graphical representation of these values to facilitate a comparison between them. Though the K_3 and K_4 values of zinc bromide and iodide are not obtained, it is expected that the overall stabilities of ZnX_4^{2-} complexes increase in the order of $I^- < Br^- < Cl^- < NCS^-$. This sequence in methanol is as same as that in water.[6] The magnitude of K_1 is also in the order of $I^- < Br^- < Cl^- < NCS^-$, while the K_2 value is in the order of $NCS^- < I^- < Br^- < Cl^-$. The variation of K_2 among the halide systems is smaller than that of K_1.

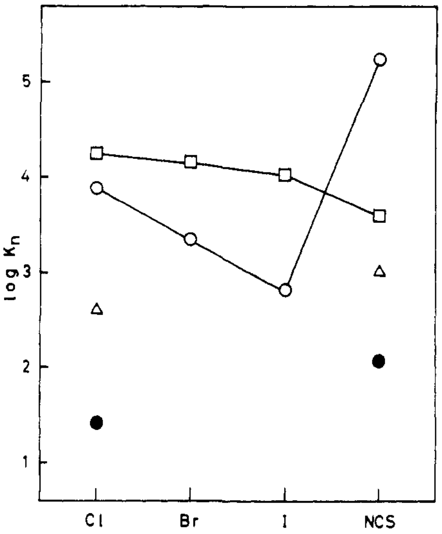

Figure 4. Stepwise thermodynamic stability constants of zinc chloride, bromide, iodide, and thiocyanate in methanol at 25.0 °C: (○) K_1; (□) K_2; (△) K_3; (●) K_4.

Now we will discuss these results with the principle of hard and soft acids and bases, the HSAB principle, suggested by Pearson.[7] In the principle, zinc(II) is a borderline element of hard and soft acids, and the softness of the ligands (the bases) increases in the order of $Cl^- < Br^- < I^- \simeq NCS^-$. This order is taken from the abscissa of Figure 4. From trends in both the K_1 values for zinc halide systems and all the K_2 values, it is clear that zinc(II) is a hard acceptor. Therefore, one may feel that an abnormally large value is obtained for the K_1 value of zinc thiocyanate and that the value is probably an exception to the trend in hardness for zinc(II). On the basis of the discussion in the previous paper,[2] however, we think that the K_1 values of zinc halides become very small because of large steric hindrance between the ligands, a halide ion and five solvated methanols, of the octahedral zinc monohalide complex. So, we believe that this difference in the K_1 values between the thiocyanate and halide complexes of zinc results from the difference in the structures of their mono X^- complexes; that is, it depends on whether or not structural changes take place in the course of the formation of their mono complexes. Thus it can be presumed that irregularities of hard and soft are closely associated with structural changes in complex formation. Also, it is certain that the borderline acids of the HSAB principle change their structures in the midst of their complex formation. With respect to the K_3 and K_4 values, it is difficult to interpret their trends using the HSAB principle because the state of a central metal changes with increasing number of ligands coordinated with it. In the

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(6) Smith, R. M.; Martell, A. E. "Critical Stability Constants"; Plenum Press: New York, 1976; Vol. 4.

(7) (a) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533–3539. (b) Pearson, R. G. *Science (Washington D.C.)* **1966**, *151*, 1721–1727. (c) Pearson, R. G. *Chem. Br.* **1967**, *3* (3), 103–107. (d) Pearson, R. G. *J. Chem. Educ.* **1968**, *45*, 581–587, 643–648.

following paragraphs, the relation between the K_1 and K_2 values of zinc halide complexes will be discussed in detail.

In the stepwise stability constants of complexes MX_nS_{N-n},[8] one expects, and generally finds, anticooperativity,[1] where M and S stand for a metal ion and a solvent molecule, respectively, and N is a maximum coordination number. In some studies,[2-4] however, strong cooperativity has been exhibited by zinc halide complexes. The cooperativity exhibited by zinc chloride complexes, which indicates $K_1 < K_2$ in our systems, has been previously explained by the structural change from octahedral $ZnXS_5^+$ to tetrahedral ZnX_2S_2.[2] The present results have affirmed our view on cooperativity. This is contrary to Ahrland's view on the same cooperativity as ours, which is made on the basis of stoichiometric ($I = 1$ M) enthalpy and entropy changes for zinc chloride and bromide complexes in dimethyl sulfoxide.[9] We have touched on this disagreement in a previous discussion.[2]

It has been reported that the free energy changes are very often more suitable for structural interpretations than the enthalpy and the entropy changes.[10] We agree because free energies give direct information on the stability of chemical species.

It is thought that the small K_1 values of zinc halides are caused by large steric hindrance between the ligands of $ZnXS_5^+$. Therefore, the K_1 value sharply decreases with coordination of the larger ligands from chloride to iodide, because the larger a ligand is, the more unstable $ZnXS_5^+$ becomes. When a solvent molecule in the octahedral $ZnXS_5^+$ is substituted by a halide ion X^-, the complex changes its conformation to the tetrahedral ZnX_2S_2. Octahedral ZnX_2S_4, if it exists, must be very crowded with the ligands and very unstable. On the other hand, the stability of the tetrahedral ZnX_2S_2, which has a relatively large space around the ligands, must not be affected so much by the size of a substituted ligand. This situation clearly appears in the results of the K_2 values of zinc halides; that is, the K_2 value gently decreases in going from chloride to iodide. Consequently, the cooperativity exhibited by zinc halide complexes in methanol steadily increases in the order of chloride < bromide < iodide.

It is interesting to discuss more deeply the change of coordination from the octahedral to the tetrahedral structure. By a step with the change, clearly, the reaction takes place with the loss of two more sovlent molecules from the sphere of coordination than that by a step without the change. Therefore, a tetrahedral species must be stable enough to compensate the energy used for the additional solvent loss, whenever the change occurs. We suggest that the structural rearrangement step of "$ZnXS_5^+$ (octahedron) $\rightleftarrows$ $ZnXS_3^+$ (tetrahedron) + 2S" does not occur though the step of "ZnX_2S_4 (octahedron) $\rightleftarrows$ ZnX_2S_2 (tetrahedron) + 2S" does. Then, the following two reasons are mainly considered. (1) The stability of octahedral species is probably more sensitive to steric hindrance between the ligands than that of tetrahedral species. Therefore, even if ZnX_2S_2 is more stable than ZnX_2S_4 with large steric hindrance, $ZnXS_3^+$ is not necessarily more stable than $ZnXS_5^+$. (2) The energy used for the solvent loss from $ZnXS_5^+$ is certainly larger than that from ZnX_2S_4. From both reasons, it seems that $ZnXS_3^+$ is not stable enough to release two solvents from $ZnXS_5^+$ and that the change is not able to occur in formation of the monohalide complex. Thus, the large K_2 is certainly caused by the favorable free energy change of the structural rearrangement of the dihalide complex.

Although we have no available information on the structures of these complexes in methanol which is given by straightforward experiments such as some diffraction methods, the existence of octahedral $Zn(CH_3OH)_6^{2+}$ and tetrahedral ZnX_4^{2-} can be inferred from analogy with data in aqueous solutions.[11] In the foregoing explanations for the cooperativity exhibited by zinc halides, it is already assumed that the $Zn(CH_3OH)_6^{2+}$ ion is octahedral. From the above discussion, it is inferred that the anticooperative zinc thiocyanate changes its structure in the course of the formation of the monothiocyanate complex; that is, the structure of the zinc monothiocyanate complex is tetrahedral $ZnNCS(CH_3OH)_3^+$ in methanol. Then, it is expected that a large K_1 results from the stable $ZnNCS(CH_3OH)_3^+$ with small steric hindrance and that the zinc thiocyanate complexes $Zn(NCS)_n(CH_3OH)_{4-n}^{2-n}$ maintain their structure in a tetrahedron until at least the tetrathiocyanate is formed. However, if there are some species coordinated by the same number of thiocyanate ions, species like octahedral $Zn(NCS)_n(CH_3OH)_{6-n}^{2-n}$, tetrahedral $Zn(NCS)_n(CH_3OH)_{4-n}^{2-n}$, and so on, which have similar stabilities in methanol, additional discussion may be necessary. In this case, the K_n defined according to eq 1 is equal to the sum of the stability constants for the individual species, and these species are indistinguishable with use of our methods. Therefore, this K_n may be somewhat large, but this entropy contribution will probably not be large enough to break the general trend in the stepwise constants. In this instance, we will probably not be able to discern the steps by which the structures are converted.

The thiocyanate ion possesses two different donor atoms of the softer S and the harder N, and the zinc(II) ion certainly coordinates via N.[12] Zinc(II) has a d^{10} electron configuration and no crystal field stabilization energy. Therefore, steric effects between ligands consume a large part of our discussion on cooperativity. If other standard thermodynamic functions, $\Delta H^\ominus$ and $\Delta S^\ominus$, become available, we will be able to discuss the structural changes in more detail. In the future, data from various spectroscopic methods and from X-ray and neutron diffraction methods will also have to be obtained in order to obtain structural information on the species in solution.

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(8) Charges are omitted for the sake of simplicity.
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