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Polymerization of Acrylonitrile-Metal Halide Complexes in the Frozen State. II. Determination of the Stability Constant of the Acrylonitrile-Zinc Chloride Complex in Aqueous Solution by Means of IR Measurement

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ABSTRACT

The stability of the $ZnCl_2$-acrylonitrile (AN) complex in aqueous solution was determined by means of IR measurements in the temperature range from 30 to -80°C. $ZnCl_2$-AN-H_2O ternary systems with compositions of 1:(1-2):(3-5) in mole ratio which were transparent and in the supercooled liquid state at low temperatures were selected for the investigation. A complex index, proposed as $D_{2270}/(D_{2270} + D_{2235})$, where D_{2235} and D_{2270} are absorbances of free AN at 2235 cm^{-1} and AN complexed with Zn cation at 2270 cm^{-1}, respectively, was determined experimentally and the stability constant of the complex was obtained from it by Bjerrum's method. The rather small value

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(2.9×10^{-3} liter^2/mole^2) of the overall stability constant at 20°C is considered due to the dissociative character of water. The stability of the complex is increased with decreasing temperature and with increasing mole fraction of $ZnCl_2$ or chlorine ion concentration in the system and the converse with increasing mole fraction of AN and/or H_2O. The 1:1 type $ZnCl_2$-AN complex is predominant at room temperature, while with decreasing temperature the 1:1 type complex is gradually converted to the 1:2 type which is a major species at -78°C. The configuration of the complex and aspects of ligand substitution are also discussed on the basis of the thermodynamic parameters.

INTRODUCTION

In a large number of complexes of nitriles with metal atoms there exists σ-bonding through the lone pair of electrons of the nitrile group. It has been found that the C≡N stretching frequency increases by about 20-80 cm^{-1} when a nitrile is coordinated to a metal through the lone pair on the nitrogen. This increase of the ν(C≡N) frequency has been observed for various complexes of acrylonitrile (AN), indicating complex formation of the nitrile with metals through the lone pair of electrons on nitrogen [1-5].

The rate enhancement of AN polymerization is attributed to this complex formation of the monomer with metals [6, 7]. In the previous paper [8], the radiation-induced polymerization of AN in frozen aqueous zinc chloride solution was carried out at low temperatures. Marked enhancement both in the rate and the degree of polymerization was observed, which indicated the importance of formation and stabilization of the complex of AN with zinc cation in the frozen medium. There appears, however, to be little direct information concerning the relationship between the enhancement of the polymerization and the actual complex concentration, because of difficulty in determination of the complex concentration.

In the present paper, in an attempt to obtain basic information for further kinetic study of this polymerization system, an IR method to determine the stability of the AN-zinc chloride complex in water was developed and also aspects of ligand substitution and the configuration of the complex are discussed on the basis of thermodynamic parameters.

EXPERIMENTAL

Materials

AN was washed successively with 5% aqueous solutions of sodium hydroxide, phosphoric acid, and distilled water and then fractionally distilled after drying over potassium carbonate. Analar grade zinc chloride, not subjected to further purification, was dried at about 150°C for more than 5 hr under reduced pressure immediately before preparation of aqueous zinc chloride solution.

Measurement of IR Spectra

The IR spectra of aqueous solutions of AN-zinc chloride complex were measured at low temperature with a Shimadzu IR-27G grating spectrometer. The sample was maintained at the appropriate temperature by means of a low-temperature IR absorption cell. The liquid sample was placed between two pieces of CaF_2 window which were mounted in a copper holder soldered to the bottom end of a copper tube, forming a coolant reservoir which was, in turn, housed in a vacuum jacket equipped with windows. Cooling of the CaF_2 windows was accomplished by liquid nitrogen. The window (CaF_2) temperature was measured by means of a copper-constantan thermocouple. Scanning was in the region of 4000-1000 cm^{-1}.

To obtain spectra of volatile compounds such as AN, benzene (BZ), and a mixture of AN and BZ, a tightly closed cell was used to prevent evaporation during scanning.

Differential Thermal Analysis

The thermal behavior of the $ZnCl_2$-AN-H_2O ternary system was examined by using a Shimadzu DTB-20 differential thermal analyzer. The sample, in an open platinum cell, was quenched with liquid nitrogen, and measurement was started from -140°C at a rate of temperature increase of about 2°C/min under a helium atmosphere, α-alumina being used as reference.

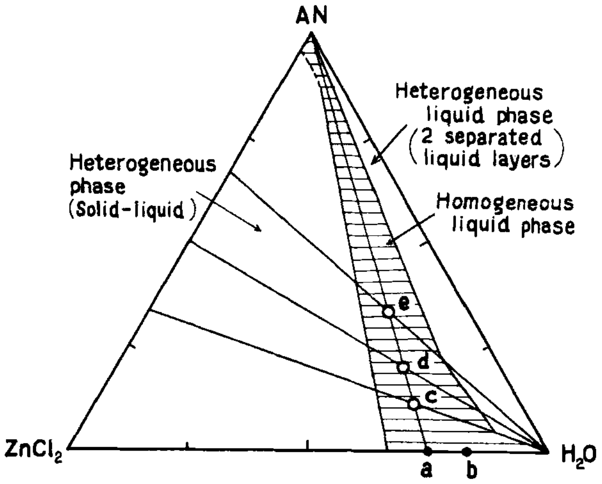

FIG. 1. Isothermal phase diagram for $ZnCl_2$-AN-H_2O ternary system at 20°C. Open circles are representative experimental compositons: (e) $ZnCl_2$:AN:H_2O = 1:2:3; (d) 1:1:3; (c) 1:0.5:3.

RESULTS AND DISCUSSION

Mutual Solubility and Thermal Behavior of $ZnCl_2$-AN-H_2O Ternary System

The mutual solubility of $ZnCl_2$-AN-H_2O ternary system was tested at 20°C, and an isothermal phase diagram is shown in Fig. 1. The phase diagram is composed of three regions: two heterogeneous phases in both sides (near the AN-H_2O and AN-$ZnCl_2$ axes) and one homogeneous solution phase in the middle of the phase diagram.

Since this investigation was designed to cover the stability of the complex in the temperature range from -78 to 30°C, differential thermal analysis (DTA) was carried out only for the homogeneous solution phase at 20°C to ascertain whether it has any thermal discontinuity such as melting, glass transition, or morphological change in this temperature range. The results of DTA are shown in Fig. 2. All samples of various composition examined were transparent, and no crystalline structure was formed by quenching with liquid nitrogen. Only one glass transition point (T_g) was observed over the entire

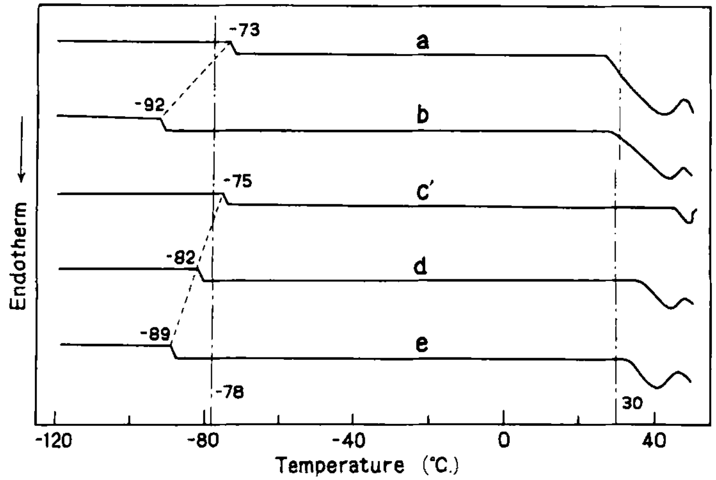

FIG. 2. Thermograms for $ZnCl_2$-AN-H_2O ternary systems of various compositions: (a) mole ratio of $ZnCl_2$:AN:H_2O 1:0:3; (b) 1:0:5; (c') 1:0.1:3; (d) 1:1:3; (e) 1:2:3.

temperature range from -140 to 30°C. The supercooled liquid state was so stable that no aging effect to produce any crystalline structure was observed, even during storage for more than one week at -78°C. The T_g of the system decreases as the mole fraction of water or AN increases. The composition having T_g higher than -78°C was excluded from this experiment. The experiments, therefore, were limited mainly to the three compositions denoted on Fig. 1.

IR Spectra of $ZnCl_2$-AN Complex

The $C\equiv N$ stretching frequency of AN (2235 cm^{-1}) shifts by 35 cm^{-1} to a higher frequency on complex formation with zinc atom in the aqueous solution. In order to obtain the complex concentration by IR measurement a relative ratio between the extinction coefficients, ϵ_{2235} and ϵ_{2270}, of absorption bands for free and complexed nitrile, respectively, and its temperature dependence must be known. There also exist two types of $ZnCl_2$-AN complex with mole ratios of $ZnCl_2$: AN = 1:1 and 1:2 [6, 7, 9]. All attempts, however, to obtain IR spectra of each type complex under an air atmosphere to determine differences between absorption bands of each type complex which are expected from their dissimilarity in composition and configuration, were unsuccessful because of the extremely high hygroscopicity of the complexes.

To determine the ratio $\alpha = \epsilon_{2270}/\epsilon_{2235}$, therefore, we used benzene solutions of $ZnCl_2$-AN complexes having 1:1:1 and 1:2:2 compositions expressed in mole ratio of $ZnCl_2$:AN:BZ. These were prepared by Hirai's procedure [10].

IR Spectra of $ZnCl_2$-AN Complex in Benzene

As shown in Fig. 3, the spectrum of the complex in benzene solution (1:2:2) at 25°C showed a shifted band at 2270 cm^{-1}. The band at 2235 cm^{-1} disappeared completely at low temperatures. The spectrum

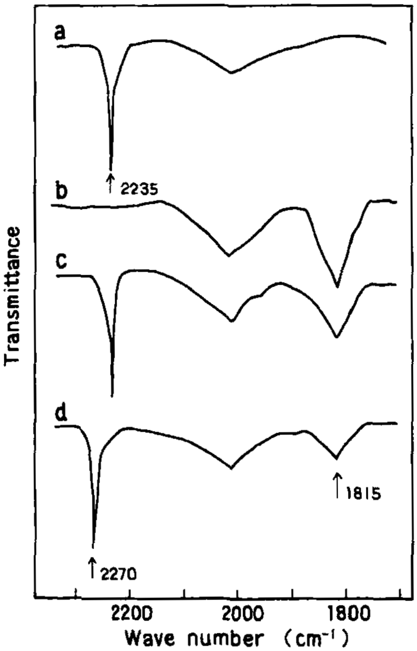

FIG. 3. IR spectra of $ZnCl_2$-AN complex in benzene and of AN in benzene solutions at 25°C: (a) pure AN, (b) pure benzene; (c) AN and benzene solution; (d) $ZnCl_2$-AN complex in benzene (1:2:2).

of the benzene solution of the complex with 1:1:1 composition was very similar in its shape and relative intensity of absorptions to that of the solution with 1:2:2 composition.

The absence of the absorption band at 2235 cm^{-1} indicates the non-dissociative character of both type complexes in benzene with those compositions. The coincidence of the absorption band at 2270 cm^{-1} of both complexes means the band shift due to complex formation is apparently independent of complex configuration and ligand number.

Provided the measurements of the absorbance of the bands at 2270 and 2235 cm^{-1}, D_{2270} and D_{2235}, respectively, are made at the same AN concentration, the relationship, $\alpha = \epsilon_{2270}/\epsilon_{2235} = D_{2270}/D_{2235}$, holds. The α value was practically determined by dividing the value D_{2270}/D_{1815} of the benzene solutions of the complexes having the compositions 1:2:2, with the value D_{2235}/D_{1815} of the AN-BZ mixture solution of 1:1 mole ratio, where D_{1815} was the absorbance of the band for out-of-plane C-H deformation of the benzene ring at 1815 cm^{-1}. If the absorbances D_{2270}, D_{2235}, and D_{1815} obey the Beer-Lambert Law, a linear relationship between the mole ratio of AN to BZ and D_{2270}/D_{1815} or D_{2235}/D_{1815} will hold in these experimental concentration range. The value D_{2270}/D_{1815} of the benzene solution of the complex with 1:2:2 composition divided by the value D_{2235}/D_{1815} of the AN-BZ mixture solution with 1:1 mole ratio, gives the value of $\alpha = D_{2270}/D_{2235}$, since the mole ratio of AN to BZ is kept constant at unity in both systems. The linearity was confirmed in the AN-BZ mixture solution in this experimental range, as shown in Fig. 4.

The values of D_{2270}/D_{1815} and α at various temperatures are shown in Fig. 5. A negative linear relationship between log α or log D_{2270}/D_{1815} and 1/T was observed at temperatures above -27.5°C, although less temperature dependence of α or D_{2270}/D_{1815} was observed below this temperature. DTA data showed that the solution in benzene of the complex of 1:2:2 composition crystallized at around -27°C, and the solidification of the system is believed to be responsible for the lack of temperature dependence of α below -27.5°C. The α values below this temperature were estimated by extrapolation of the α curve to lower temperatures, shown in Fig. 5 as a dotted line. This estimation should be valid for the $ZnCl_2$-AN-H_2O systems which are still in the supercooled liquid state below this temperature. The α values obtained at various temperatures are listed in Table 1 and are used later for correcting complex concentrations observed.

IR Spectra of $ZnCl_2$-AN Complex in Water

As the complex is dissolved in water, both absorption bands at 2235 and 2270 cm^{-1} appear, as shown in Fig. 6. The coexistence of two

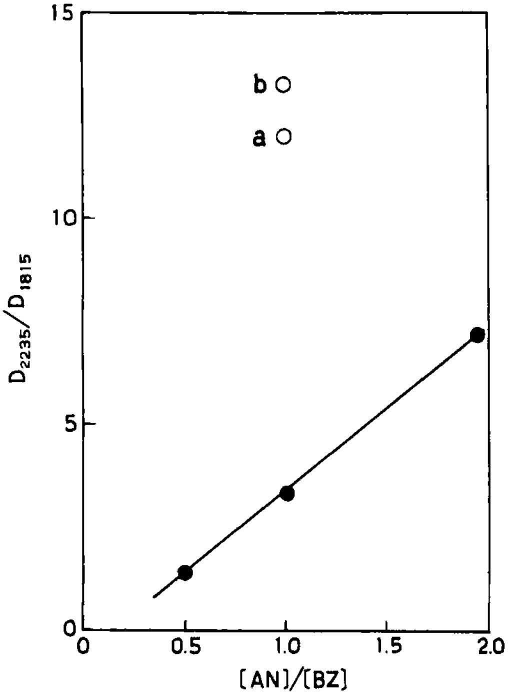

FIG. 4. Plot of D_{2235}/D_{1815} as a function of [AN]/[BZ] in AN-benzene mixture: (○) D_{2270}/D_{1815} values for the complexed AN with compositions of $ZnCl_2$:AN:BZ of (a) 1:1:1 and (b) 1:2:2.

absorption bands implies that the complex is partly dissociated to some extent until equilibrium between complexed AN and free AN is attained.

The absorbances of both absorption bands were sensitive to changes in the composition of the solution and temperature. The value D_{2270}/D_{2235} increased as the mole fraction of $ZnCl_2$ increased, while it decreased with increasing mole fraction of AN and/or H_2O. A larger value of D_{2270}/D_{2235} resulted at lower temperatures, as shown in Fig. 6.

Based on these facts mentioned above, a new index, the "complex index," defined as $J = D_{2270}/(D_{2270} + D_{2235})$ is proposed as a measure of complex concentration. Figure 7 is a plot of the complex index J against 1/T in the temperature range from -78°C to 30°C. It is evident from

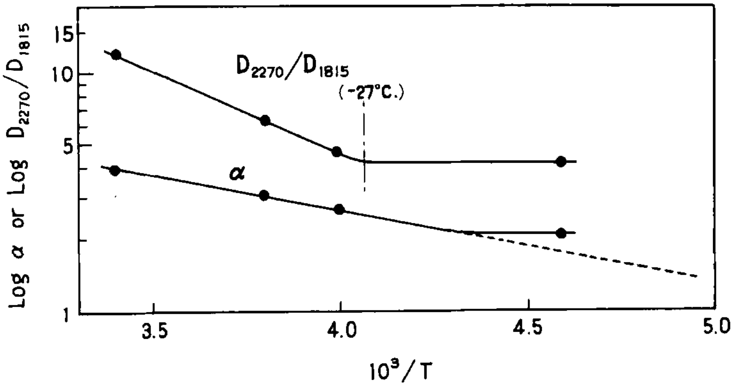

FIG. 5. Temperature dependence of α and D_{2270}/D_{1815} for the system of $ZnCl_2$:AN:BZ = 1:2:2.

TABLE 1. Dependence of α on Temperature

Temperature (°C)	α
30	4.30
20	3.91
0	3.25
-20	2.69
-40	2.10
-60	1.58
-80	1.11

Fig. 7 that the complex index can be expressed as a linear function of 1/T, that is, the lower the temperature, the higher the values of the complex index. A larger extent of dependence of the complex index on 1/T was seen with increasing mole fraction of H_2O, and a smaller dependence was obtained as the value $\gamma = [ZnCl_2]/[AN]$ became larger or smaller. The maximum extent of the dependence was observed when the γ value was between 0.5 and 2.0. The complex

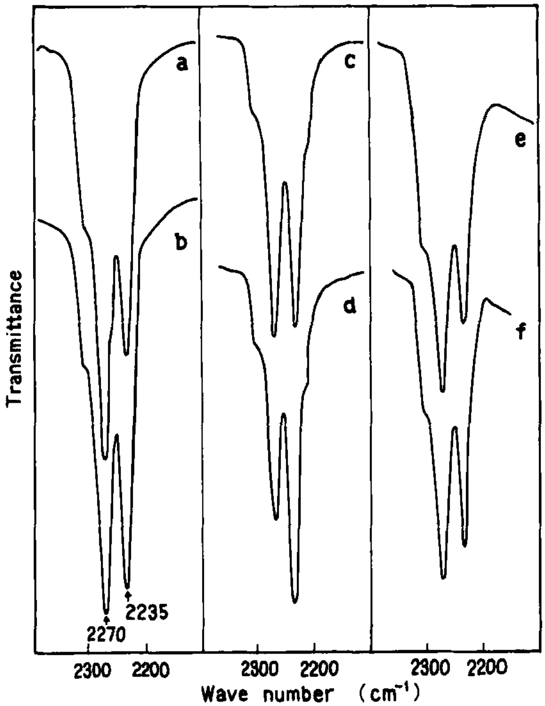

FIG. 6. IR spectra of $ZnCl_2$-AN-H_2O ternary systems at various compositions and temperatures: (a) 1:1:3, 25°C; (b) 1:2:3, 25°C; (c) 1:1:5, 25°C; (d) 1:2:5, 25°C; (e) 1:2:3, -62°C; (f) 1:2:3, -18°C.

index at the same temperature increased as the mole fraction of H_2O or AN decreased, and the opposite tendency was observed with decreasing mole fraction of $ZnCl_2$.

Determination of Stability Constants of $ZnCl_2$-AN Complex in Water

Assuming the Beer-Lambert Law is valid and that only 1:1 and 1:2 type complexes are formed in the system, we have

$$D_{2235} = \epsilon_A [A] L \tag{1}$$

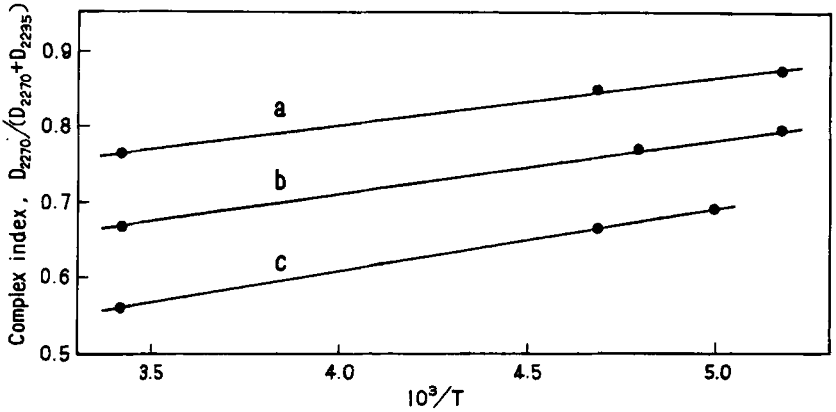

FIG. 7. Temperature dependence of complex index, $D_{2270}/(D_{2270} + D_{2235})$, at various compositions of $ZnCl_2$:AN:H_2O (a) 1:0.5:3; (b) 1:1:3; (c) 1:2:3.

$$D_{2270} = (\epsilon_1[C]_1 + 2\epsilon_2[C]_2)L \tag{2}$$

where $[A]$, $[C]_1$, $[C]_2$ are the concentrations and ϵ_A, ϵ_1, and ϵ_2 are the extinction coefficients of free AN at 2235 cm^{-1}, of the 1:1 type complex at 2270 cm^{-1}, and of the 1:2 type complex at 2270 cm^{-1}, respectively, and L is the path length of the cell. Then the complex index J becomes

$$\begin{aligned} J &= D_{2270}/(D_{2270} + D_{2235}) \\ &= (\epsilon_1[C]_1 + 2\epsilon_2[C]_2)/(\epsilon_A[A] + \epsilon_1[C]_1 + 2\epsilon_2[C]_2) \end{aligned} \tag{3}$$

Obtaining $\alpha = \epsilon_1/\epsilon_A$ from the experiment, assuming $\epsilon_1 = \epsilon_2$ and putting these relations into Eq. (3), we then have

$$J = \alpha([C]_1 + 2[C]_2)/\{[A] + \alpha([C]_1 + 2[C]_2)\} \tag{4}$$

The concentration of free AN in the system, therefore, is calculated as

$$[A] = [A]_0\alpha(1 - J)/\{\alpha(1 - J) + J\} \tag{5}$$

where $[A]_0$ is the total concentration of AN.

Since $[A]$ can be estimated from J and α values as mentioned above, the stability constants of the complex are determined in a way similar to Bjerrum's method [11] as follows:

$$M + A \overset{k_1}{\rightleftharpoons} MA$$

$$k_1 = [MA]/[M][A] \tag{6}$$

$$MA + A \overset{k_2}{\rightleftharpoons} MA_2$$

$$k_2 = [MA_2]/[MA][A] \tag{7}$$

$$M + 2A \overset{K}{\rightleftharpoons} MA_2$$

$$K = [MA_2]/[M][A]^2 \tag{8}$$

The average number $\bar{n}$ of ligands per metal atom is expressed as

$$\bar{n} = ([MA] + 2[MA_2])/[M] + [MA] + [MA_2]) \tag{9}$$

therefore,

$$\bar{n} \doteq (k_1[A] + 2k_1k_2[A]^2)/(1 + k_1[A] + k_1k_2[A]^2) \tag{10}$$

where $[M]$, $[MA]$, and $[MA_2]$ are concentrations of free metal cation, 1:1 type complex, and 1:2 type complex, respectively. Stepwise and overall stability constants, k_1, k_2, and K can be calculated from the Eq. (10), since the $\bar{n}$ value is obtained from the J and α values, total concentrations of metal cation and AN, $[M]_0$ and $[A]_0$, respectively, as follows:

$$\bar{n} = ([A]_0 - [A])/[M]_0$$

$$= [A]_0 J/[M]_0 \{\alpha(1 - J) + J\} \qquad (11)$$

Therefore, the solution of more than two simultaneous equations established at different compositions gives the values of stepwise stability constants k_1 and k_2.

Stability Constants and Thermodynamic Parameters

The stability constants, k_1 and k_2, of the $ZnCl_2$-AN complex in water at various temperatures ranging from -80 to 30° C were obtained from the solution of simultaneous equations as explained in the preceding section and listed in Table 2. The overall stability constant K was obtained as a cross product of k_1 and k_2 values. The rather small magnitude of the K values obtained is considered due to the dissociative character of water as a solvent. Only a few other stability constant data for AN-metal complexes have hitherto been reported: for the $SnCl_4$-AN complex, $k_1 = 2.0$ and $k_2 = 1.0$ liter/mole at 20-25° C in benzene [12]; for $AlEtCl_2$- and $AlEt_2Cl$-AN complexes, K = 117 and 38 liter/mole, respectively, in methylene chloride [13].

With respect to the temperature dependence of the stability constants, as shown in Fig. 8, a striking feature is a sharp inflection of both the k_1 and k_2 curves at -62° C, that is, the slope of k_1 goes from a positive to a negative value, while a steeper slope of the k_2 curve results. Consequently, the constant slope of K in whole temperature range is maintained.

It should be noted that the stability constants obtained here are rather rough approximate estimates because of the peculiar system examined where the concentrations of solutes (AN, $ZnCl_2$) are high and the Beer-Lambert Law might not be completely valid. Although there exists such a limitation, apparent thermodynamic constants were calculated and are listed in Table 2.

The enthalpy changes ΔH_1 and ΔH_2 were obtained from the slopes of temperature dependence curves of k_1 and k_2 (Fig. 8) and the free energy changes ΔG_1 and ΔG_2 and the entropy changes ΔS_1 and ΔS_2 were calculated from the equations, $-RT \ln k = \Delta G$ and $\Delta G = \Delta H - T\Delta S$, respectively. The free energy changes ΔG_1 and ΔG_2 are successively decreased with lowering temperature over the whole temperature range higher than -62° C. This fact indicates that the increase in complex stability with decreasing temperature is due

TABLE 2. Stability Constants and Thermodynamic Parameters of $ZnCl_2$-AN Complex in H_2O[a]

Temp (°C)	k_1 (liter/ mole)	k_2 (liter/ mole)	K (liter^2/ mole^2)	ΔG_1 (kcal/mole)	ΔG_2 (kcal/mole)	ΔS_1 (e. u.)	ΔS_2 (e. u.)
30	0.113	0.0193	0.0022	1.31	2.38	-7.84	-22.6
20	0.120	0.0245	0.0029	1.24	2.16	-7.83	-22.6
0	0.137	0.0415	0.0057	1.08	1.73	-7.84	-22.7
-20	0.160	0.0754	0.0121	0.922	1.30	-7.84	-22.8
-35	0.183	0.125	0.0229	0.804	0.984	-7.84	-22.9
-40	0.192	0.152	0.0291	0.765	0.874	-7.84	-22.9
-60	0.238	0.343	0.0816	0.608	0.453	-7.84	-23.1
						Avg. -7.84	Avg. -22.8
-70	0.223	0.646	0.144	0.606	0.177	+1.76	-31.5
-80	0.197	1.46	0.287	0.804	-0.145	+1.75	-31.5
						Avg. +1.76	Avg. -31.5

[a] ΔH_1: above -62°C, -1.06 kcal/mole; below -62°C, +0.963 kcal/mole. ΔH_2: above -62°C, -4.47 kcal/mole; below -62°C, -6.23 kcal/mole.

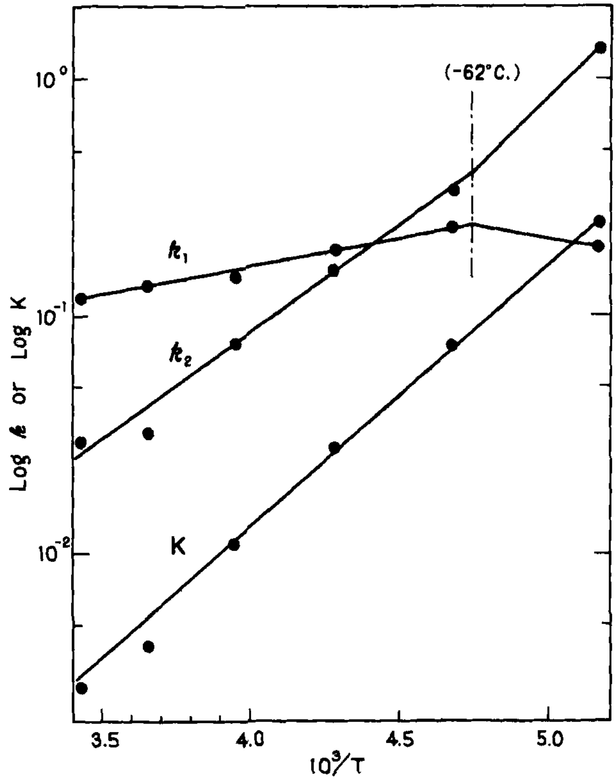

FIG. 8. Temperature dependence of stability constants of $ZnCl_2$-AN complex in H_2O.

mainly to the exothermic nature of complex formation between Zn atom and AN at temperatures higher than -62°C. The drastic change in the enthalpy and entropy changes at -62°C is considered a reflection of the change both in the complex configuration and in the competitively substituting ligands.

Three ligand species, i.e., AN, H_2O, and Cl^-, coexist in this system, and the competition for ligands is thought to be significantly affected by temperature. Ultraviolet spectroscopic analysis was carried out in order to clarify the ligand substitution at various temperatures and compositions in the solution of $ZnCl_2$-AN complex in H_2O. As shown in Fig. 9, a broad absorption peak with a λ_{max}

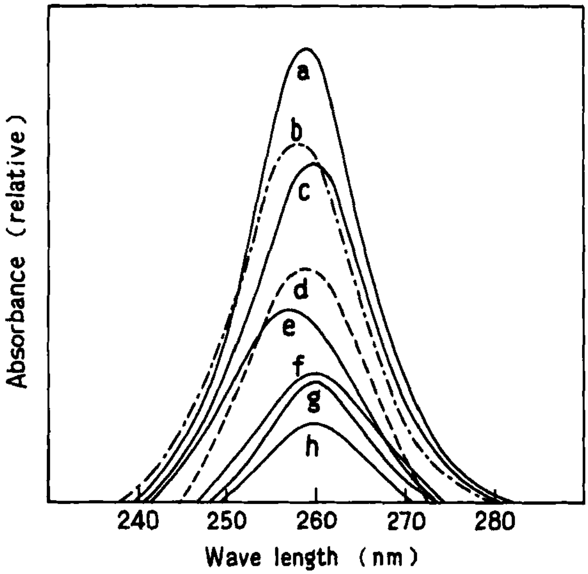

FIG. 9. Difference UV spectra of aqueous $ZnCl_2$-AN complex solutions with various compositions at 20 and -78°C, the compositions being expressed as mole ratio of $ZnCl_2$:AN:H_2O(:HCl): (a) 1:0:3:0.1, 20°C; (b) 1:0:3, -78°C; (c) 1:0:3, 20°C; (d) 1:0.1:3:0.1, 20°C; (e) 1:0.1:3, -78°C; (f) 1:0.1:3, 20°C; (g) 1:0:5, -78°C; (h) 1:0:5, 20°C.

from 258 to 260 nm was observed. According to the UV investigation on the aqueous $ZnCl_2$ solution [14], the absorption with a maximum at 260 nm was attributed to the zinc-chloro complex (presumably a di- or trichloro complex). Furthermore, coexistence of NH_4Cl was reported to result in the formation of the tetrachloro complex, $[ZnCl_4]^{2-}$, with an absorption maximum at 271 nm. There is other evidence for the formation of the zinc-chloro complex in aqueous solution [15-21].

This peculiar absorption peak, however, was sensitively diminished when the mole ratio Y of H_2O was larger than 5, regardless of the mole ratio X of AN in the $ZnCl_2$-AN-H_2O ternary system, where the composition is expressed in the mole ratio as 1:X:Y. The absorbance of the absorption peak increased sharply with decreasing mole fraction of H_2O, accompanied by only negligible shift of the peak.

A similar change of the absorption peak was also observed with changing temperature of the system, that is, sensitive increase in absorbance and a slight red shift when the system was cooled to -80°C, which is just above the glass transition temperature of the system. The increased stability of the zinc-chloro complex at low temperatures can be reasonably explained by the exothermic nature of the zinc-chloro complex formation [14] on replacement of H_2O with Cl^-. An increase in absorbance at 260 nm and a slight red shift of the peak was also observed with addition of HCl to the concentrated aqueous $ZnCl_2$ solution of the 1:0:3 system.

In these experiments, the red shift above 260 nm was not observed in the concentrated aqueous $ZnCl_2$ solution, even with cooling or addition of HCl to the system. Thus it seems that no tetrachlorozinc complex is formed. Therefore, the species responsible for the absorption at 260 nm is identified as a di- or trichloro complex.

The decrease in the absorbance at 260 nm with the addition of AN indicates that AN mainly replaces Cl^- in the formation of the $ZnCl_2$-AN complex. This explains the higher complex index value obtained in the presence of HCl. With cooling of the system, an increase in the absorbance at 260 nm in the aqueous zinc chloride solution and a higher value of the complex index in the ternary system are noted. Thus it is concluded that two factors contribute to the higher stability of the $ZnCl_2$-AN complex at lower temperatures: an increase in the concentration of the zinc-chloro species and the exothermic nature of the Zn-AN complex formation.

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