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Spectrophotometric investigations of the complexation between Ni(II) and thiocyanate in aqueous methanol

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Abstract

Ni(II) adds up to three thiocyanate ligands per cation in water and aqueous methanol. All three of the observed complexes are green, the color characteristic of free Ni(II) perchlorate, consistent with the absence of any geometry change occurring upon complexation. Equilibrium constants were obtained as a function of temperature and solvent composition. Because the magnitude of the third complex was significantly lower than for the first two species, the Benesi–Hildebrand method was used to measure the third complexation constant.

1. Introduction

The competition between solvent and ligand for a metal ion center is of fundamental importance in understanding the structures, thermodynamics and kinetics of metal ion complexes in solution. The principles to determine successive equilibrium constant data were published in a classic paper by Jannik Bjerrum [1], which involved the use of the glass electrode. In the decades since then, metal ion complexation studies have been carried out using a variety of techniques.

Our interest in metal ion complexation equilibria was based upon our ultrasonic relaxation work detecting geometry changes in lanthanide [2] and zinc(II) [3] systems. In order to determine if a kinetic technique, like ultrasonic absorption, can detect geometry changes as we hypothesized, we went back to the postulated octahedral–tetrahedral geometry changes found by Swift [4] using temperature jump to study Co(II) and Ni(II) thiocyanate systems. Using a spectrophotometric method, we detected an octahedral–tetrahedral change in the Co(II)-thiocyanate system accompanying the addition of the fourth ligand [5], although this change was under different conditions from the one postulated by Swift. In DMF, Ishiguro [6] found a similar Co(II) octahedral–tetrahedral change, but it was initiated upon the addition of the third isothiocyanato ligand to the metal ion and was also found for the fourth complex. This demonstrates that the solvent can have a major impact on geometry changes, and that the effect can be steric, or due to the solvent donor properties, hydrogen bonding or other effects.

The results for the reaction of Ni(II) with thiocyanate are not as clear as for Co(II) with the same ligand. In DMF [6], no color change was found and this was interpreted as the absence of a geometry change in all species up to $[Ni(NCS)_4(DMF)_2]^{2-}$. Bonding between the ligand and the metal ion center was predicted to occur via the hard nitrogen end. The Ni(II)-isothiocyanato system has also been studied in water using techniques as diverse as stopped flow, IR and UV–Vis absorption spectroscopy. The earliest measurement was by Fronœus using cation exchange at 20 °C and an ionic strength of 1.0, finding the first complexation constant (K_1) to be 15.0 ± 0.5, the second complexation constant (K_2) to be 2.94 and the third (K_3) to be 1.48 [7]. Tribalat [8] and Landers [9] found a fourth complexation constant. Bjerrum [10,11] found four complexes at the limit of zero ionic strength and 25 °C, with $K_1 = 13.8$, $K_2 = 3.8$, $K_3 = 1.05$ and $K_4 = 0.12$. Bjerrum states that because the fourth equilibrium constant is so small, it cannot be determined by the normal methods of

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equilibrium constant determinations using a fixed ionic strength. Currently, there are many studies in water involving mixed complexes of nickel(II)-thiocyanate with other ligands and there are studies of these complexes in thin films [12], micellar solutions [13] and in electrochemistry [14]. Ni(II) complexation with thiocyanate has also been studied in acetone [15], in DMF [6,16], in *N*,*N*-dimethylacetamide (DMA) [17], and in methanol [18,19]. In DMF, the two studies gave different results for the octahedral complexes with only mono- and dithiocyanate complexes in the first [16], and up to four thiocyanate ligands bound in the other study [6]. The acetone study found both octahedral and tetrahedral complexes with one, two, three or six thiocyanate ligands bound per Ni(II) ion [15]. Up to four ligands were bound per Ni(II) in DMA, but there were also two structural isomers with different numbers of bound waters [17]. In methanol, Ragulin [18] found the first three complexes, whereas Khan found only the mono- and dithiocyanato complexes [19].

Questions exist if the complexation changes are primarily a function of dielectric constant differences, solvent steric effects, or solvent donor number. This research project in aqueous methanol was initiated shortly after the completion of the Co(II) study [5] to determine if a coordination number/geometry change can occur and be detected in the Ni(II)-thiocyanate system.

2. Experimental

2.1. Materials

Hydrated nickel(II) perchlorate (GFS Chemicals), sodium perchlorate (GFS Chemicals), and sodium thiocyanate (Aldrich) were used without further purification. Methanol (Aldrich Spectrophotometric Grade) was also used without any purification. Because we worked in aqueous methanol, the methanol was not dried before use. Stock solutions of $Ni(ClO_4)_2$ and $NaClO_4$ were made by weight in water or methanol. However, since we did not determine the numbers of bound and associated waters each time a stock solution was made, the Ni(II) was standardized gravimetrically using dimethylglyoxime and/or by EDTA titration using murexide as an indicator for each stock solution. Whenever possible, below 90% methanol/10% water solutions, the stock solutions of $Ni(ClO_4)_2$ and $NaClO_4$ were prepared in water. Dried NaSCN was weighed directly into each volumetric flask. Because of possible decomposition, the solutions were discarded after a few hours.

2.2. Solutions

Experiments were carried out at 15, 20, 25 and 37 °C in water and in methanol/water mixtures containing 20%, 40%, 60%, 80% and 90% methanol by volume. The correct volume of methanol was added to each volumetric flask along with the reagents, and then the flask was diluted to the mark using water. Beer's law plots were carried out on the $Ni(ClO_4)_2$ solutions at each temperature and solvent composition to determine the extinction coefficients for free Ni(II) at the wavelengths 396, 659 and 721 nm. Beer's law was valid for nickel perchlorate, but deviations from Beer's law were found when NaSCN was added, attributed to the formation of one or more complexes. The spectral behavior of the Ni(II)-thiocyanate solutions at the absorption wavelengths was more similar to the lanthanides than to most d-block transition metal systems, in that the complexes did not shift wavelengths, rather their extinction coefficients changed. The ionic strength was maintained at 0.5 with the $NaClO_4$ stock solutions. In order to estimate the $NaClO_4$ needed, a short spreadsheet calculation was performed with literature values for the three complexation constants. After the conclusion of the studies, the results for solutions which deviated from the ionic strength by more than 5% were discarded and new test solutions were made with better guesses for the complexation constants.

2.3. Calculations

We used a pc program developed by Gaizer [20–22] to determine the extent of complexation and the equilibrium constants using multiple wavelengths. We have modified this program using the program QUICK BASIC to make it more user friendly and to speed up the calculation time. The program assumes the existence of one or more complexes of the type M_pL_q, with the stability constants defined as

$$\beta_{pq} = [M_pL_q]/[M]^p[L]^q. \quad (1)$$

At each wavelength, it is assumed that Beer's law is valid for each chemical species and that the absorbances are additive. At the wavelengths used in this study, neither perchlorate nor thiocyanate absorbed. Although this program is most efficient when the free metal and the complexes absorb at different wavelengths, it can be used for systems where all species absorb at the same wavelengths, but there is a small difference in the extinction coefficients. To use this program, the stability constants and the extinction coefficients for each species are estimated and the program minimizes the square of the residuals, calculating the best β values and extinction coefficients. Because the magnitude of the third complexation constant (K_{13}) is small compared to that for the monothiocyanato species (K_{11}) and the dithiocyanato species (K_{12}), the Gaizer program calculations could neither establish the existence of the third complex, nor could it provide reliable values for K_{13}.

We were able to determine the stability constants for the third complex in each solvent mixture by using the Benesi–Hildebrand method [23], originally developed to study the reactions of iodine with aromatic hydrocarbons. In these experiments, difference spectra are obtained, with the reference solution containing the metal ion, ionic media, and the same solvent as the test solution, which differs only in having the ligand, thiocyanate, present [5]. The experiment uses matched 1.00 cm cells (Helma). If M_o and L_o represent the total concentration of Ni(II) and SCN, respectively, and if the third complex is symbolized by ML_3, the complexation constant is given by

$$\begin{aligned} K_{13} &= [ML_3]/[ML_2][L] \\ &= [ML_3]/(M_o - [ML_3])(L_o - [ML_3]). \end{aligned} \tag{2}$$

We have assumed that the second complex is the dominant species present in solution at large excesses of thiocyanate ion. Under the conditions of excess ligand, $L_o \gg$ complex, and the expression simplifies to

$$K = [ML_3]/(M_o - [ML_3])(L_o). \tag{3}$$

Substituting the absorbance difference, $\Delta A = \Delta\varepsilon$ b $[ML_3]$, we can replace $[ML_3]$ by $\Delta A/\Delta\varepsilon$ in matched cells where $b = 1.00$ cm, obtaining:

$$K = (\Delta A/\Delta\varepsilon)/(M_o - (\Delta A/\Delta\varepsilon))(L_o). \tag{4}$$

Algebraic manipulation yields:

$$1/\Delta A = (1/M_o K \Delta\varepsilon L_o) + (1/M_o \Delta\varepsilon). \tag{5}$$

Thus, a plot of $1/\Delta A$ as a function of $1/L_o$ gives a straight line with an intercept equal to $(1/M_o\ \Delta\varepsilon)$ and a slope equal to $(1/M_o K_{13} \Delta\varepsilon)$, thereby allowing the calculation of the complexation constant by dividing the intercept by the slope. If more than one complex is present, then systematic deviations from linearity occur at low values of $1/L_o$. The Benesi–Hildebrand plots were consistent with the formation of the third complex.

3. Results and discussion

The solutions made from $Ni(ClO_4)_2$ in water or aqueous methanol were green, a color which is typical of octahedral hexaquo nickel(II) complexes. The addition of small or large amounts of thiocyanate did not change the green color. If the addition of thiocyanate would have changed the color from green to yellow, that would have been an indication of a geometry change, since yellow is the color characteristic of a square planar complex like $Ni(CN)_4$. Thus, the addition of SCN^- does not appear to cause any geometry change even as we add up to three thiocyanates per Ni(II) ion. Fig. 1 shows the spectra of 0.100 M $Ni(ClO_4)_2$ and 0.100 M $Ni(ClO_4)_2$ with 0.100 M NaSCN in water at 25 °C. The addition of the thiocyanate, shown in Fig. 1, does not change the absorption wavelengths of the free or complexed Ni(II). The inset in Fig. 1 is the calculated difference spectrum and once again no new peaks are detected. An equivalent spectrum was obtained when the spectrophotometer was used with the sample containing thiocyanate in the sample chamber and the sample without thiocyanate in the reference chamber. This is different than the observations using Co(II), where the addition of the third thiocyanate ligand caused a color change from pink to blue, due to an octahedral–tetrahedral geometry change [5]. For all aqueous methanol solutions at each of the four temperatures, the addition of thiocyanate increases the absorbance as shown in Fig. 2, a plot of the absorbance at constant ionic strength and constant Ni(II) concentration in one solvent mixture as a function of ligand concentration. Even at a ratio of thiocyanate to Ni(II) of 4.3 to 1, the graph has not yet leveled off to show complete addition of the second ligand. Fig. 3 is a plot of the absorbance data at 396 nm in each of the experimental solvent mixtures. As the methanol content increases in the solvent mixtures, the absorbance increases, consistent with an increase in the presence of

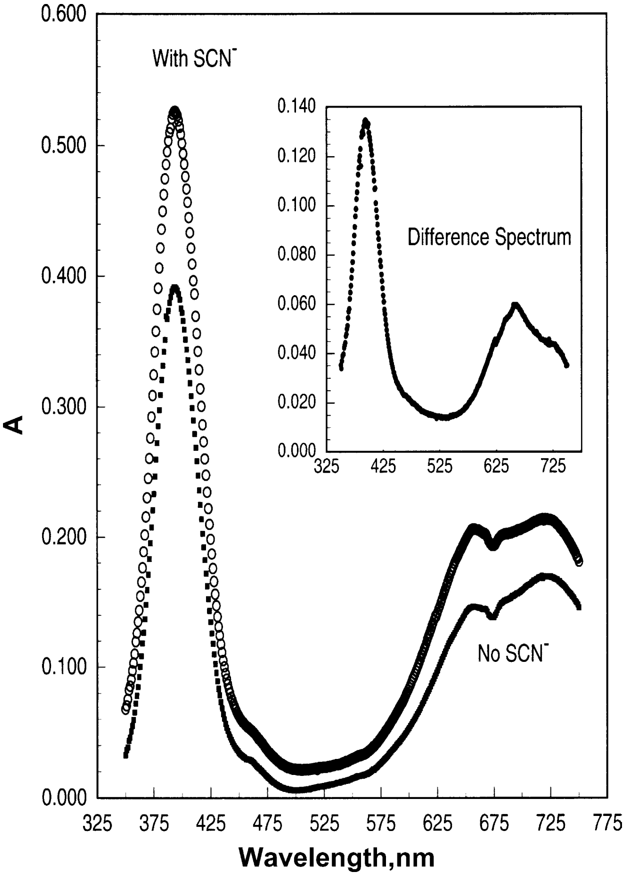

Fig. 1. The absorption spectra for 0.100 M $Ni(ClO_4)_2$ and 0.100 M Ni(II) with 0.100 M NaSCN in water at 25 °C. The inset is the difference spectrum and the titles of the axes are the same as for the large graph.

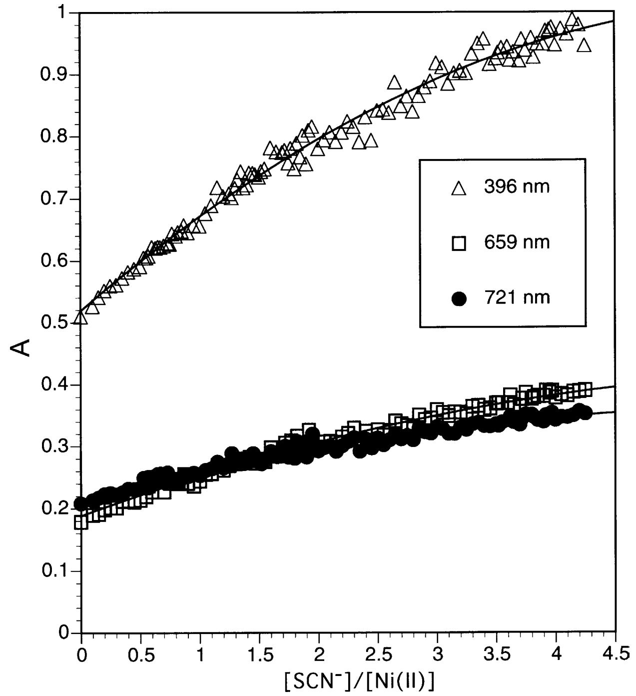

Fig. 2. The absorbance as a function of thiocyanate to nickel concentration ratios in 20% methanol–80% water at 25 °C at 396, 659 and 721 nm.

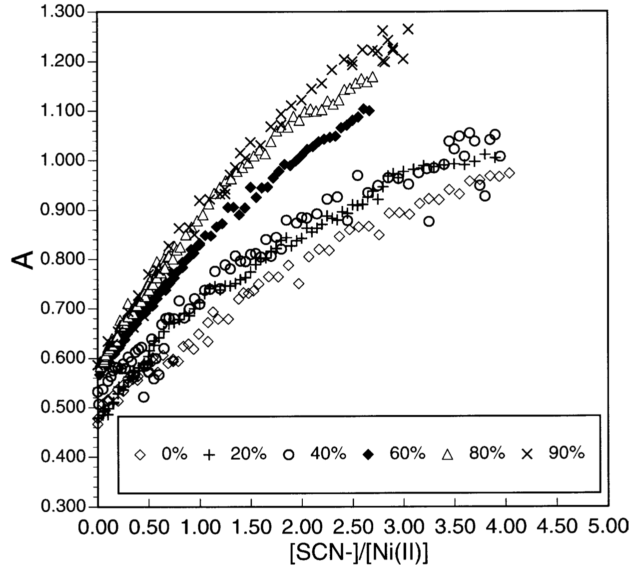

Fig. 3. The absorbance as a function of thiocyanate to nickel concentration ratios at 396 nm and 25 °C as a function of the percent methanol in the solvent mixtures. The absorbance increases as the percent methanol increases.

Ni(II)-thiocyanate complexes, since each of the complexed nickel species has a higher extinction coefficient than the free nickel. Although none of the curves levels off, as would have resulted from complete complexation of the nickel, the data come closest in the 90% methanol/10% water solutions.

The data could not be fitted using the Gaizer program assuming the formation of but a single complex, $[NiSCN]^+$. The addition of a second species, $[Ni(SCN)_2]$ improved the fit. The program works by fixing one or more of the complexation constants; the best fits for the individual extinction coefficients for each species are calculated; then U, defined as

$$U = \sum (A_{\text{experimental}} - A_{\text{calculated}})^2, \tag{6}$$

is calculated for the fixed complexation constants; and then a new value of β_i is chosen and the cycle is repeated. Fig. 4 is a typical plot of U as a function of log β is developed and the minimum is the best fit for log β. For perfect data, the plot will resemble the letter "V" and the closer it resembles the letter "U", the greater the uncertainty in the value of log β. With poor data or the wrong number of complexes, the U plot does not rise from the minimum. For best results, data below a ligand to metal ion ratio of 0.5–0.7 are used to calculate β_1, which is identical to K_{11}, given by

$$\beta_{11} = K_{11} = [\mathrm{ML}]/[\mathrm{M}][\mathrm{L}]. \tag{7}$$

When the best fits for β_{11} are obtained, then a ligand to metal ion ratio up to 1.7 is used to calculate β_{12}, given by

$$\beta_{12} = K_{11}K_{12} = [\mathrm{ML_2}]/[\mathrm{M}][\mathrm{L}]^2. \tag{8}$$

Attempts to calculate β_{13} using all of the data either did not work, or gave results for the numerical value of β_{13} that were significantly too high to not have reached a maximum value of the absorbance in Fig. 3. In order to dramatically increase the thiocyanate/nickel ratio at ionic strength of 0.5, we reduced the Ni(II) concentration by an order of magnitude to 0.0100 M and we were able to obtain almost a 300:1 ratio of thiocyanate to nickel. Due to the low value of K_{13} compared to β_{12}, the

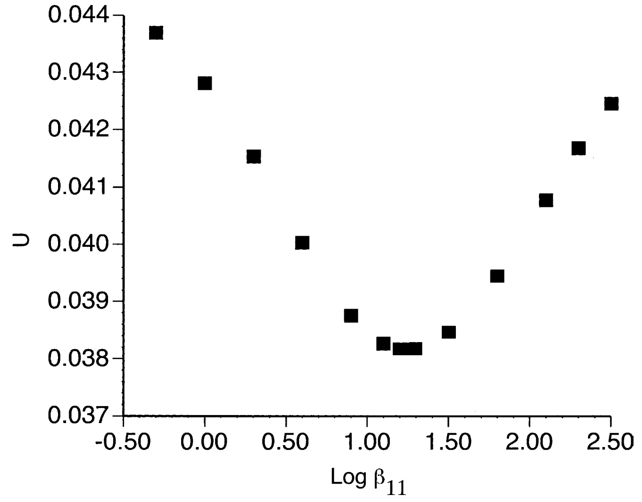

Fig. 4. The U plot for Ni(II)/SCN⁻ in 60% methanol/40% water at 15 °C for the determination of the first equilibrium constant. The minimum is the best value for β_{12}.

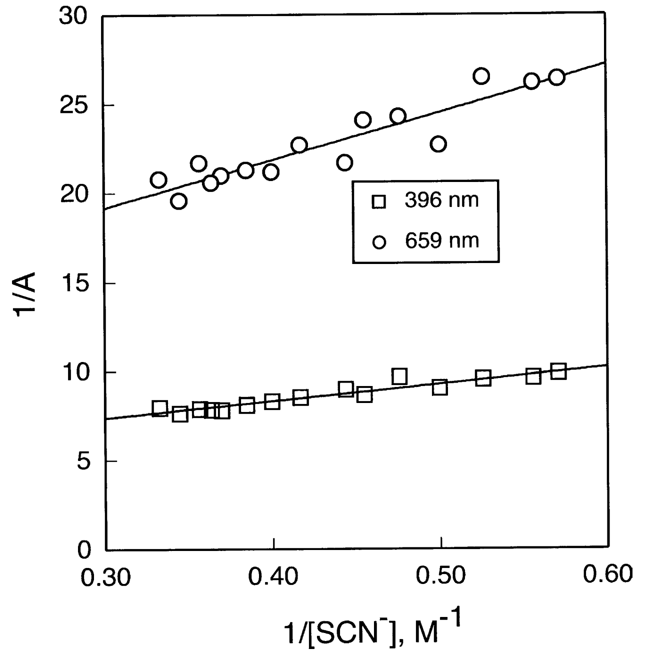

Fig. 5. The Benesi–Hildebrand plot at 25 °C in 20% methanol and 80% water. The [Ni(II)] is 0.0100 M in all of the solutions. *K* is calculated from the intercept divided by the slope. For these measurements the ionic strength could not be held constant.

Gaizer program still was unable to yield a good fit of the experimental data at any of the solvent conditions studied. For that reason we went to the Benesi–Hildebrand method [23] that we have successfully used in other systems [24,25]. Typical Benesi–Hildebrand results are shown in Fig. 5. If a fourth complex was present at the highest ratios of [SCN^-]/[Ni(II)], there would have been systematic deviations from linearity at the lowest 1/[SCN^-] values, and these were absent. Thus we are able to estimate the values of K_{13} as a function of solvent and temperature. The calculated values for the equilibrium constants are summarized in Table 1 and Fig. 6. We note the relatively large percent errors reported in Table 1.

We attempted to calculate the enthalpies and entropies of complexation for each successive step by using the standard van't Hoff method of plotting the log of each successive stability constant as a function of temperature. The van't Hoff Equation is:

$$\ln K = -\Delta H^\circ/RT + \Delta S^\circ/R. \qquad (9)$$

However, because of the relatively small changes in the thermodynamic parameters in $\log K$ as a function of temperature, coupled to the reported errors in each equilibrium constant, gave uncertainties that were too large to obtain meaningful enthalpy and entropy results in most solvent mixtures. For those whose enthalpies were near zero, the uncertainty in the enthalpy is such that the sign of the function was not determined. The cause for these errors is the observation that only the

Table 1

The complex formation constants for Ni(II)–SCN^- as a function of temperature and aqueous methanol solvent mixtures

% Water	15 °C			20 °C			25 °C			37 °C		
	K_{11}	K_{12}	K_{13}	K_{11}	K_{12}	K_{13}	K_{11}	K_{12}	K_{13}	K_{11}	K_{12}	K_{13}
100	18.2 ± 1.3	4.3 ± 0.3		19.1 ± 1.8	4.7 ± 0.4		20.0 ± 1.7	4.5 ± 0.4		19.5 ± 1.8	5.0 ± 0.5	
80	24.5 ± 0.6	34.7 ± 4.8	0.48 ± 0.17	31.6 ± 1.5	31.6 ± 5.1	0.42 ± 0.18	26.9 ± 0.6	46.8 ± 7.6	0.43 ± 0.30	25.7 ± 1.8	13.8 ± 2.9	0.37 ± 0.20
60	22.9 ± 1.1	24.6 ± 3.4	0.39 ± 0.22	17.4 ± 0.8	30.9 ± 6.5	0.44 ± 0.29	20.4 ± 0.9	19.5 ± 4.1	0.45 ± 0.27	22.4 ± 1.0	15.9 ± 3.3	0.38 ± 0.30
40	46.8 ± 2.2	20.4 ± 2.8	0.50 ± 0.30	100 ± 9	20.0 ± 4.6	0.47 ± 0.30	19.1 ± 0.9	15.5 ± 4.0	0.49 ± 0.27	138 ± 16	44.7 ± 11.4	0.48 ± 0.29
20	158 ± 33	102 ± 59	0.60 ± 0.15	100 ± 12	120 ± 51	0.56 ± 0.27	126 ± 17	105 ± 58	0.54 ± 0.33	56.2 ± 5.2	66.1 ± 20.1	0.54 ± 0.31
10	178 ± 16	77.6 ± 18.0	0.91 ± 0.28	309 ± 36	79.4 ± 22.2	0.65 ± 0.36	151 ± 14	229 ± 64	0.68 ± 0.34	229 ± 26	120 ± 37	0.59 ± 0.41

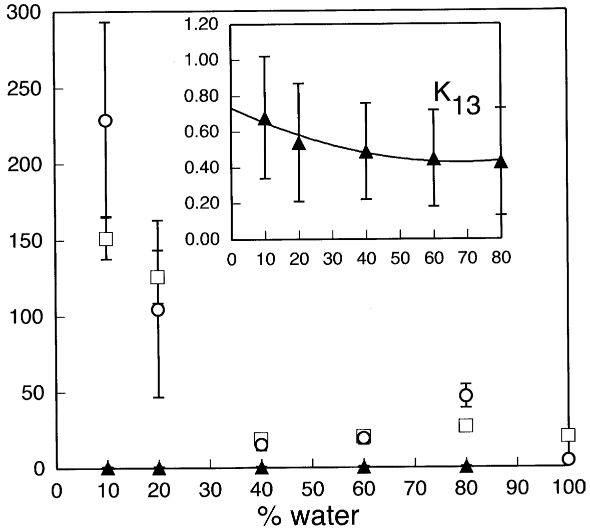

Fig. 6. The variations on the Ni(II)–SCN$^-$ complexation constants at 25 °C as a function of the percent water. The K_{13} curve is the inset and the axes are the same as for the large graph. Key: □, K_{11}; ○, K_{12}; △, K_{13}.

extinction coefficients changed during complexation, not the absorption wavelengths.

In summary, we have determined that the addition of thiocyanate does not cause an octahedral/square planar geometry change, consistent with the absence of a color change from green to yellow. In water at 25 °C, K_{11} was determined to be 20.0 ± 1.7 and K_{12} was 4.5 ± 0.4. Although both constants are higher than the earlier reported range, the K_{12} result is close to the earlier range of 2.94–3.8. The earlier K_{11} results had a range of 13.8–15. Considering the differing ionic strengths and experimental techniques, the agreement is acceptable. Three complexes were found in each water/methanol solvent mixture. We have characterized the equilibrium constants as a function of solvent and temperature (Table 1). As expected, the complexation constant increases as the dielectric constant for the solvent mixture decreases. Thus, we can conclude that in water or aqueous methanol, Co(II) changes geometry in the presence of thiocyanate, but under the same conditions Ni(II) does not.

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