The Ethoxyacetate and (Ethylthio)acetate Complexes
of Nickel(II)

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The formation of ethoxyacetate and (ethylthio)acetate complexes
of nickel(II) has been studied in aqueous solution by determining the
concentration of free ligand in the complex solutions. The investiga-
tion has been performed at 25.0°C in a perchlorate medium at an
ionic strength of 1 M.

In an earlier investigation of the stepwise formation of copper(II) complexes
of ethoxyacetate and (ethylthio)acetate ions [1] it was found that chelates
are formed to a much higher extent by the latter ligand than by the former.
This should indicate that the affinity of the copper(II) ion for an oxygen atom
in the ether position is less than for a sulphur atom in the same position.

Yasuda *et al.*[2] have reported values of the stability constants of the 1:1
complexes between several central ions and oxydiacetate and thiodiacetate
ions, respectively. For the copper(II) complexes they found a much larger
stability constant for the thio-compound than for the corresponding oxo-
compound, which points in the same direction as the findings mentioned
above. Also for the nickel(II) ion they report a considerably higher stability
of the complex with the thio-compound than of the one with the oxo-com-
pound.

The investigation reported here has been carried out in order to find out
if a similar effect exists with ligands which should act at most as bidentate.

The complex systems were studied by determining the concentration of
free ligand in the complex solutions. This determination was made indirectly
by measuring the hydrogen ion concentration in buffer solutions containing
the ligand and its corresponding acid. The buffers had a pH-value of about 4.
It was found during the measurements that the protolysis of the hydrated
nickel(II) ion could be neglected at this pH.

At an early stage it was clear that the complexity in the systems under
investigation was rather weak. In such a case it is essential that the data upon
which the calculations are based are subject to only small errors, if reliable
stability constants are to be calculated. Therefore all measurements were
made four times and the calculations based on the mean values.

## THE PRINCIPLES FOR CALCULATION OF THE STABILITY CONSTANTS.

The stability constants have been calculated according to a method by Fronæus.[3,4] The following brief presentation only deals with equations used in the present investigation.

Consider first the case that only mononuclear complexes ML_n are formed between the central ion M and the ligand L. The maximum number of ligands coordinated by a central ion in the system is denoted by N. With the total concentrations of central ion and ligand denoted by C_M and C_L, respectively, the following equations hold

$$C_M = [M] + [M] \sum_{n=1}^{N} \beta_n [L]^n \qquad (1)$$

$$C_L = [L] + [M] \sum_{n=1}^{N} n \ \beta_n [L]^n \qquad (2)$$

where the gross stability constant $\beta_n = [ML_n]/([M][L]^n)$ is the equilibrium constant for

$$M + n \ L \ \rightleftharpoons \ ML_n$$
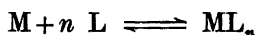
From eqn. (1) it is found that the quantity $C_M/[M]$ is a polynomial in [L]. This polynomial is denoted by X and its derivative by X′.

$$X = 1 + \sum_{n=1}^{N} \beta_n [L]^n \qquad (3)$$

$$X' = \sum_{n=1}^{N} n \ \beta_n [L]^{n-1} \qquad (4)$$

The mean number of ligands coordinated by a central ion in a certain solution is denoted by $\bar{n}$

$$\bar{n} = (C_L - [L])/C_M \qquad (5)$$

Using eqns. (1)−(4), the eqn. (5) can be rewritten in the forms

$$\bar{n} = [L] \ X'/X \qquad (6)$$

or

$$\bar{n}/[L] = X'/X \qquad (7)$$

From eqn. (3) it is clear that the β_n-values should easily be obtained if the X-values corresponding to the experimentally determined [L]-values can be calculated. This can be done by integrating eqn. (7) which leads to

$$\ln X \ ([L]_j) = \int_{0}^{[L]_j} (\bar{n}/[L]) \ d[L]$$

This integral can be evaluated graphically from a plot of $\bar{n}/[L]$ against [L].

Thus, corresponding values of X and [L] are obtained. The determination of the stability constants β_n can now be performed either numerically, e.g. by application of the least-squares principle, or graphically by successive extrapolation to [L] = 0 of the functions

$$X_j = (X_{j-1} - \beta_{j-1})/[L]; \quad (1 \leq j \leq N; \quad X_0 = X; \quad \beta_0 = 1)$$

If both mononuclear and dinuclear complexes are formed it can be shown [3] that $\bar{n}/[L]$ is a function of both $[M]$ and $[L]$. For decreasing C_L the limit value of $\bar{n}/[L]$ takes the form

$$\lim_{C_L \to 0} (\bar{n}/[L]) = \beta_1 + C_M \ \beta_{12} \tag{8}$$

where

$$\beta_{12} = [M_2L]/([M]^2[L])$$

From eqn. (8) it is evident that an increase of C_M should cause an increase of $\bar{n}/[L]$ for small values of $[L]$ if dinuclear complexes are formed.

CALCULATIONS FROM EXPERIMENTAL DATA

In the investigation the hydrogen ion concentration was determined in the complex solutions ($[H_3O^+]$ denoted by h_M), and in solutions with the same stoichiometric concentration C_L' of ligand but with $C_M = 0$ ($[H_3O^+]$ denoted by h_0). The solutions were obtained by mixing suitable volumes of stock solutions of ionic strength 1 M, viz.

1: 0.333 M $Ni(ClO_4)_2$ with free acid concentration $= \alpha \times 0.333$ M.
2: A buffer solution of 1.000 M NaL and δ M HL.
3: 1.000 M $NaClO_4$ with free acid concentration $= h_s$ (M).

For the weak acid HL it was presupposed that the acid constant, K_a, defined by

$$K_a = [H_3O^+][L]/[HL]$$

should have the same value, independent of C_M, in solutions with constant C_L'. This leads to the following expression for the concentration of free ligand in the complex solutions

$$[L] = \frac{h_0}{h_m} \ (C_L' - s_0 + h_0) \ \frac{\delta C_L' + \alpha C_M + s_m - h_m}{\delta C_L' + s_0 - h_0} \tag{9}$$

where s_0 and s_m are due to the excess of free acid in the stock solution of sodium perchlorate. In the present case they are

$$s_0 = h_s \ (1 - C_L') \quad \text{and} \quad s_m = h_s \ (1 - C_L' - 3 \ C_M)$$

According to eqn. (5) $\bar{n}$ is obtained by

$$\bar{n} = (C_L' - \alpha C_M - s_m + h_m - [L])/C_M \tag{10}$$

EXPERIMENTAL

Chemicals

Nickel(II) perchlorate was prepared from analytical grade nickel carbonate and perchloric acid. The product was recrystallized several times from water. The concentration of nickel in the stock solution was found to be (0.333 ± 0.001) M by spectrophotometric titration with EDTA.[5] The titration was performed at 990 mμ using a Beckman Model B spectrophotometer furnished with a magnetic stirrer. By potentiometric titrations with perchloric acid essentially according to a method described earlier,[1]

a small deficit of acid was established in the stock solution. In this way α was found to be -2×10^{-4}. No foreign ions could be detected in the stock solution.
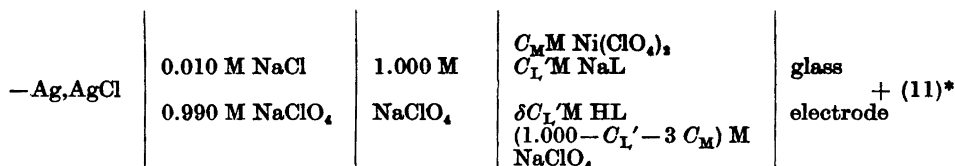
Ethoxyacetic acid and *(ethylthio)acetic acid* were supplied by Eastman Organic Chemicals. The equivalent weights were found to be 104.2 and 120.5, respectively (calc. 104.1 and 120.2, respectively). The acids were used without further purification. Carbonate free sodium hydroxide was used in preparing buffer solutions, which were analysed by means of a cation exchange resin in the hydrogen form. The acid constants at 25°C and $I = 1.00$ M were determined by potentiometric titrations. For the ethoxyacetic acid was found $K_a = (3.08 \pm 0.04)$ M, and for the (ethylthio)acetic acid $K_a = (2.25 \pm 0.02)$ M, in good agreement with values earlier obtained for carefully purified preparations.[6]

The same *sodium perchlorate* preparation was used as in an earlier investigation.[6] Thus h_s in eqn. (9) had the value -3.8×10^{-5} M.

All other chemicals were of analytical grade.

Method

In the main investigation the emf of cells of the following type was measured.

$$-\text{Ag,AgCl} \left| \begin{array}{c} 0.010 \text{ M NaCl} \\ \\ 0.990 \text{ M NaClO}_4 \end{array} \right| \begin{array}{c} 1.000 \text{ M} \\ \\ \text{NaClO}_4 \end{array} \left| \begin{array}{c} C_M \text{M Ni(ClO}_4)_2 \\ C_L' \text{M NaL} \\ \delta C_L' \text{M HL} \\ (1.000 - C_L' - 3\,C_M) \text{ M} \\ \text{NaClO}_4 \end{array} \right| \begin{array}{c} \text{glass} \\ \text{electrode} \end{array} \quad + \text{ (11)}*$$

This emf is denoted by E' if $C_M \neq 0$ and by E'' if $C_M = 0$. In practice the measurements were arranged as titrations at constant C_M. The solutions in the right hand half cell were obtained by mixing known volumes of two solutions S_1 and S_2.

	S_1 C_M	S_2 C_M^0	
Ni(ClO$_4$)$_2$	C_M	C_M^0	M
NaL	0	C_L^0	M
HL	0	δC_L^0	M
NaClO$_4$	$1.000 - 3\,C_M$	$1.000 - 3\,C_M - C_L^0$	M

Effective mixing was obtained by a magnetic stirrer. Stable emf readings were reached within a few minutes. Oxygen-free nitrogen was passed through all solutions containing (ethylthio)acetate to prevent oxidation of the ligand.

To check the constancy of the asymmetry potential of the glass electrode the emf E_R of the cell (12) was measured before and after each titration.

$$\text{RE} \left| \begin{array}{c} \text{ethoxyacetate buffer} \\ [\text{H}_3\text{O}^+] = h_R \\ \text{NaClO}_4 \text{ to } I = 1.000 \text{ M} \end{array} \right| \begin{array}{c} \text{glass} \\ \text{electrode} \end{array} \qquad (12)$$

The quantities h_m and h_0 in eqn. (9) were calculated from

$$E_M = E' - E_R = 59.16 \log (h_m/h_R) \quad \text{mV}$$
$$E_0 = E'' - E_R = 59.16 \log (h_0/h_R) \quad \text{mV}$$

Obviously the quotient h_0/h_m can be calculated directly from

$$E_L = E' - E'' = E_M - E_0 = -59.16 \log (h_0/h_m) \quad \text{mV}$$

The glass electrode used in this investigation was a Beckman 40495, the slope of which was found to be the theoretical (59.2 mV/pH) in the pH-range $2.4 \leq \text{pH} \leq 4.5$. The emf was read by a Radiometer PHM 4 potentiometer. The Ag/AgCl reference electrode was prepared according to Brown.[7] The entire cell was thorougly thermostated to $(25.00 \pm 0.05)°\text{C}$ and the emf was reproducible in general within ± 0.2 mV.

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* The left hand half cell including the salt bridge is in this paper denoted by RE.

Table 1. Determination of corresponding values of [L] and $\bar{n}/[L]$ in the nickel(II) ethoxyacetate system. The values of E_0 refer to $h_R = 8.10 \times 10^{-5}$ M.

C_L' mM	E_0 mV	$C_M = 80.0$ mM			$C_M = 60.0$ mM			$C_M = 40.0$ mM		
		E_L mV	[L] mM	$\frac{\bar{n}}{[L]}$ M⁻¹	E_L mV	[L] mM	$\frac{\bar{n}}{[L]}$ M⁻¹	E_L mV	[L] mM	$\frac{\bar{n}}{[L]}$ M⁻¹
1.417	−9.2	11.4	0.837	10.6	9.1	0.951	10.4	7.1	1.059	11.2
3.46	−3.0	13.4	1.973	10.5	10.8	2.222	10.5	7.9	2.531	10.6
6.67	−0.9	14.3	3.73	10.4	11.6	4.19	10.5	8.3	4.81	10.4
9.64	−0.1	14.5	5.40	10.3	11.8	6.04	10.4	8.3	6.97	10.2
12.41	0.2	14.7	6.91	10.3	11.8	7.78	10.3	8.3	8.97	10.0
17.81	0.6	14.7	9.96	10.1	11.7	11.24	10.0	8.2	12.93	9.7
21.82	0.6	14.7	12.23	10.0	11.8	13.73	10.0	8.3	15.78	9.8
29.23	0.7	14.6	16.47	9.8	11.6	18.56	9.7	8.2	21.23	9.6
34.6	0.7	14.5	19.6	9.7	11.6	22.0	9.7	8.0	25.3	9.3
40.3	0.7	14.4	22.9	9.6	11.4	25.8	9.5	8.0	29.5	9.3
56.3	0.6	14.0	32.6	9.2	11.2	36.4	9.2	7.8	41.6	9.0
81.4	0.3	13.3	48.5	8.6	10.5	54.1	8.5	7.2	61.5	8.1
104.8	−0.1	12.9	63.4	8.2	10.1	70.7	8.1	7.0	79.8	7.9
147.1	−0.7	11.9	92.5	7.4	9.4	102.0	7.4	6.3	115.1	7.0
201.2	−1.6	10.9	131.6	6.6	8.4	145.1	6.5	5.7	161.2	6.2
246.5	−2.4	10.1	166.3	6.0	7.9	181.2	6.0	5.3	200.6	5.7
296.6	−3.2	9.3	206.5	5.5	7.1	225.0	5.3	4.7	247.0	5.0
338	−4.0	8.9	239	5.2	6.8	259	5.1	4.5	284	4.8
380	−4.6	8.3	275	4.8	6.3	297	4.6	4.1	324	4.3
422	−5.4	8.0	309	4.6	6.0	334	4.4	4.0	361	4.2
475	−6.4	7.4	356	4.2	5.6	382	4.1	3.8	410	4.0
543	−7.6	6.8	417	3.8	5.2	444	3.7	3.4	476	3.5
613	−8.9	6.2	482	3.4	4.8	509	3.4	3.2	541	3.3
679	−10.2	5.8	542	3.2	4.4	572	3.1	2.9	607	3.0
760	−11.6	5.0	626	2.7	3.9	653	2.7	2.6	687	2.7

MEASUREMENTS

The nickel(II) ethoxyacetate system. In the main investigation of this system a buffer with $\delta = 0.265$ was used. The experimental results are collected in Table 1. Measurements were also made at $C_M = 20$ mM. The E_L-values, however, were so small as to cause a considerable scatter in the calculated $\bar{n}/[L]$-values. Since they added nothing of value to the other information in hand, these measurements were not used in the calculations.

On plotting $\bar{n}/[L]$ against $[L]$ it was found that the $\bar{n}/[L]$-values were independent of C_M. This is illustrated in Fig. 1 for smaller $[L]$-values. Thus only mononuclear complexes seemed to be formed. A smooth curve was drawn to fit all the points as well as possible. The curve was extrapolated to $[L] = 0$ giving a preliminary estimate of $\beta_3 = 10.6$ M^{-1}. Using the smooth curve, values of the X-function were obtained by graphical integration to suitable $[L]$-values (see Table 2).

Table 2. X-values obtained by graphical integration of the $\bar{n}/[L]$-function for the nickel(II) ethoxyacetate system.

[L] mM	X([L])	X_1 M^{-1}	X_2 M^{-2}	X_3 M^{-3}
0	*1*	*10.5*	*32*	*17*
5.00	1.053	10.7		
10.00	1.108	10.8		
20.00	1.224	11.2		
30.0	1.345	11.5		
40.0	1.473	11.8		
50.0	1.609	12.2		
65.0	1.824	12.7		
80.0	2.05	13.2		
100.0	2.39	13.9		
120.0	2.75	14.5	33	
140.0	3.13	15.2	34	
170.0	3.77	16.3	34	
200.0	4.51	17.6	36	
250.0	5.88	19.5	36	
300	7.47	21.6	37	17
350	9.34	23.8	38	17
400	11.45	26.1	39	18
450	13.80	28.4	40	18
500	16.43	30.9	41	18
550	19.33	33.3	41	16
600	22.52	35.9	42	17
650	25.96	38.4	43	17

To obtain an estimate of the accuracy in the determination of the β_n-values, limiting curves were drawn in the plot of $\bar{n}/[L]$ against $[L]$. On these curves the entire graphical procedure was repeated.

The determination resulted in:

$$\beta_1 = (10.5 \pm 0.3) \ \text{M}^{-1}$$
$$\beta_2 = (32 \quad \pm 3 \quad) \ \text{M}^{-2}$$
$$\beta_3 = (17 \quad \pm 6 \quad) \ \text{M}^{-3}$$

To check if complex formation occurred between the central ion and free ethoxyacetic acid, measurements were made at $C_M = 60$ mM using a buffer with $\delta = 0.421$. As can be seen from Fig. 1 no such complex formation was indicated.
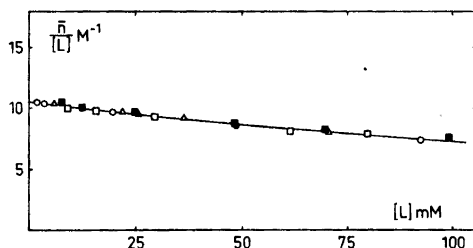

Fig. 1. Some of the $\bar{n}/[\text{L}]$-values for smaller [L] in the ethoxyacetate system. The main investigation: $C_M = 80$ mM (O), $C_M = 60$ mM ($\triangle$), $C_M = 40$ mM ($\square$). Buffer with $\delta = 0.421$, $C_M = 60$ mM ($\blacksquare$). The full-drawn curve is calculated from the β_n-values obtained in this investigation.
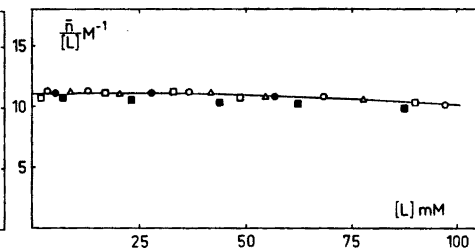
Fig. 2. Some of the $\bar{n}/[\text{L}]$-values for smaller [L] in the (ethylthio)acetate system. The main investigation: $C_M = 80$ mM (O), $C_M = 60$ mM ($\triangle$), $C_M = 40$ mM ($\square$), $C_M = 20$ mM ($\bullet$). Buffer with $\delta = 0.493$, $C_M = 60$ mM ($\blacksquare$). The full-drawn curve is calculated from the β_n-values obtained in the investigation.

Since $\bar{n}/[\text{L}]$ was independent of both C_M and δ the conclusion was drawn that the protolysis of the hydrated nickel(II) ion could be neglected in the relevant pH-range.

The nickel(II) (ethylthio)acetate system. For this system the stability constant of the 1:1-complex in 50 % dioxane has been reported by Irwing and Fernelius.[8]

The buffer used in the main part of the present investigation had a δ-value of 0.245. The experimental results are collected in Table 3.

The $\bar{n}/[\text{L}]$-values were independent of C_M, which is shown in Fig. 2 for smaller [L]-values. This indicates that dinuclear complexes are not formed in the system.

Measurements were also made at $C_M = 60$ mM using a buffer with $\delta = 0.493$. These measurements were repeated only once. As can be found from the plot in Fig. 2 the $\bar{n}/[\text{L}]$-values were somewhat smaller than those found with the other buffer. Since the difference was within the limits of experimental error, it was concluded that the free (ethylthio)acetic acid did not act as a ligand.

The graphical determination of the stability constants gave the result:

$$\beta_1 = (\ 11.0 \pm 0.3) \ \text{M}^{-1}$$
$$\beta_2 = (\ 65 \quad \pm 3 \quad) \ \text{M}^{-2}$$
$$\beta_3 = (190 \quad \pm 30 \ ) \ \text{M}^{-3}$$

Table 3. Determination of corresponding values of [L] and $\bar{n}/[L]$ in the nickel(II) (ethylthio)acetate system. The values of E_0 refer to $h_R = 8.16 \times 10^{-5}$ M.

C_L'	$-E_0$	$C_M = 80.0$ mM			$C_M = 60.0$ mM			$C_M = 40.0$ mM			$C_M = 20.0$ mM		
		E_L	$[L]$	$\frac{\bar{n}}{[L]}$	E_L	$[L]$	$\frac{\bar{n}}{[L]}$	E_L	$[L]$	$\frac{\bar{n}}{[L]}$	E_L	$[L]$	$\frac{\bar{n}}{[L]}$
		mV	mM	M⁻¹	mV	mM	M⁻¹	mV	mM	M⁻¹	mV	mM	M⁻¹
1.788	16.6	13.9	0.974	12.0	11.2	1.112	11.8	7.6	1.320	10.8	4.4	1.532	11.3
2.942	14.0	14.5	1.606	11.4	11.3	1.854	10.8	8.1	2.136	10.7	4.6	2.487	11.1
4.62	12.5	15.1	2.50	11.3	11.9	2.86	10.9	8.5	3.31	10.8	4.6	3.89	10.6
6.76	11.8	15.5	3.63	11.3	12.3	4.14	11.0	8.8	4.78	10.9	4.9	5.61	11.1
9.77	11.2	15.7	5.23	11.2	12.3	6.01	10.8	8.9	6.90	10.8	4.8	8.14	10.7
14.84	11.0	16.1	7.86	11.3	12.8	8.97	11.2	9.2	10.36	11.1	5.1	12.20	11.3
24.50	10.8	16.2	12.97	11.3	12.8	14.84	11.0	9.3	17.04	11.1	5.1	20.12	11.2
33.9	10.8	16.3	17.92	11.3	12.9	20.5	11.0	9.3	23.6	11.2	5.1	27.9	11.1
47.5	11.0	16.4	25.0	11.3	13.0	28.6	11.1	9.4	32.9	11.1	5.1	39.0	11.1
69.1	11.3	16.3	36.6	11.2	13.0	41.6	11.1	9.1	48.5	10.7	5.0	56.9	10.8
89.4	11.6	16.2	47.5	11.1	12.7	54.5	10.7	9.1	62.7	10.7	4.7	74.5	10.1
126.7	12.4	15.9	68.2	10.8	12.5	77.9	10.5	8.8	89.9	10.3	4.7	105.5	10.1
175.4	13.3	15.2	97.0	10.1	11.8	110.8	9.7	8.0	128.5	9.2	4.2	149.0	8.9
217.1	14.3	14.9	121.5	9.8	11.4	139.3	9.3	7.7	160.9	8.8	4.1	185.1	8.7
264.3	15.3	14.1	152.6	9.2	10.6	174.9	8.5	7.1	200.5	8.0	3.9	227.1	8.2
304	16.2	13.4	180.4	8.6	10.1	205	8.0	6.7	234	7.5	3.5	265	7.3
346	17.2	12.8	210	8.1	9.5	239	7.5	6.4	269	7.1	3.3	304	6.9
380	17.8	11.9	239	7.4	8.8	270	6.8	5.9	302	6.5	2.9	340	6.0
427	18.9	11.2	276	6.8	8.4	308	6.5	5.6	343	6.1	2.8	383	5.8
479	20.2	10.6	317	6.4	7.9	352	6.0	5.2	391	5.6	2.8	430	5.8
538	21.4	9.7	369	5.7	7.2	406	5.4	4.7	448	5.0	2.4	490	4.9
603	23.1	8.9	427	5.2	6.8	463	5.1	4.5	506	4.8			
679	24.8	7.9	499	4.5	6.0	537	4.4	4.0	581	4.2			
760	26.6	6.9	581	3.9	5.4	616	3.9	3.4	666	3.5			

DISCUSSION

The maximum $\bar{n}$-value calculated from the measurements was about 1.8 in the ethoxyacetate system and about 2.4 in the (ethylthio)acetate system. This is illustrated in Figs. 3 and 4. Hence it follows that at least two complexes should be formed in the former system and three in the latter.
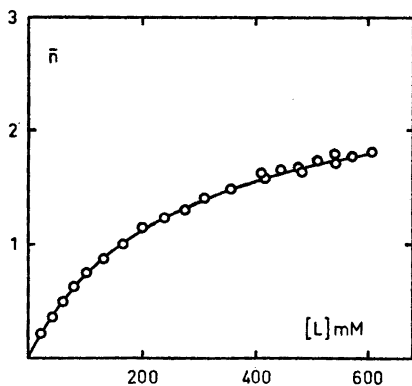

Fig. 3. Some of the experimentally obtained $\bar{n}$-values in the ethoxyacetate system (O). The full-drawn curve represents $\bar{n}$ as calculated from eqn. (6) using the β_n-values obtained in the present investigation.
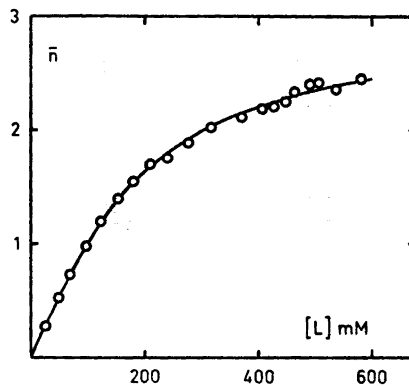
Fig. 4. Some of the experimentally obtained $\bar{n}$-values in the (ethylthio)acetate system (O). The full-drawn curve is obtained from eqn. (6) by means of the calculated β_n-values.

The graph of the X_1-function for the ethoxyacetate system could be perfectly approximated by a straight line for $[L] < 100$ mM. This indicates that only the first and the second complexes are formed in this region. The graph of the X_1-function for the (ethylthio)acetate system, however, showed a marked curvature for $[L] > 30$ mM. This indicates the presence of at least a third complex in the region $[L] < 100$ mM.

The X_2-functions could be calculated for $[L] > 200$ mM in the ethoxyacetate system and for $[L] > 100$ mM in the (ethylthio)acetate system and the plots proved to be perfectly straight lines. The β_2-values obtained from these plots agreed well with the values obtained from the slope of the X_1-functions. In both systems the X_3-function was constant (see Tables 2 and 4) and of the same value as the slope of the corresponding X_2-plot.

Thus the graphical treatment showed that three mononuclear complexes are formed in both systems in the $[L]$-range covered by these measurements. The same result was obtained by a numerical treatment using an electronic computer. In the ethoxyacetate system, however, the stability constant for the third complex is very small, and the third complex is not indicated until $[L]$ has reached a rather large value. The measured voltage E_L, upon which the calculation is founded, becomes rather small at higher values of $[L]$. Thus it may be subject to a significant systematic error caused by the liquid

Table 4. X-values from the graphical integration of the $\bar{n}$/[L]-function for the nickel(II) (ethylthio)acetate system.

[L] mM	X([L])	$\begin{matrix}X_1\\ M^{-1}\end{matrix}$	$\begin{matrix}X_2\\ M^{-2}\end{matrix}$	$\begin{matrix}X_3\\ M^{-3}\end{matrix}$
0	1	11.0	65	190
4.00	1.045	11.3		
6.00	1.068	11.4		
8.00	1.092	11.5		
10.00	1.117	11.7		
13.00	1.154	11.9		
16.00	1.194	12.1		
20.00	1.248	12.4		
25.0	1.320	12.8		
30.0	1.395	13.2		
100.0	2.95	19.5	85	
120.0	3.59	21.6	88	190
140.0	4.33	23.8	91	190
170.0	5.67	27.5	97	190
200.0	7.32	31.6	103	190
250	10.79	39.2	113	190
300	15.31	48	122	190
350	20.97	57	132	190
400	27.91	67	141	190
450	36.3	79	150	190
500	46.4	91	160	190
550	58.3	104	169	190
600	71.8	118	178	190

junction potential. Such an error does not necessarily interfere with the experimental fact that the $\bar{n}$/[L]-values are independent of C_M. Thus it may be concluded that the experimental evidence from this investigation is not sufficiently cogent as to the formation of a third complex in the ethoxyacetate system.

The stability constants β_n are collected in Table 5 together with the stepwise stability constants $K_n = [ML_n]/[ML_{n-1}][L]$.

Table 5. The calculated stability constants.

System	$\begin{matrix}\beta_1\\ M^{-1}\end{matrix}$	$\begin{matrix}\beta_2\\ M^{-2}\end{matrix}$	$\begin{matrix}\beta_3\\ M^{-3}\end{matrix}$	$\begin{matrix}K_1\\ M^{-1}\end{matrix}$	$\begin{matrix}K_2\\ M^{-1}\end{matrix}$	$\begin{matrix}K_3\\ M^{-1}\end{matrix}$	K_1/K_2	K_2/K_3
Ni^{2+}-ethoxyacetate	10.5	32	(17)[a]	10.5	3.0	(0.5)	3.4	(6)
Ni^{2+}-(ethylthio)acetate	11.0	65	190	11.0	5.9	2.9	1.9	2

[a] *cf.* the discussion.

The picture is quite different from the one found with the copper(II) complexes of the ligands in question.[1] Both nickel systems show a rather weak complexity and the quotients K_1/K_2 and K_2/K_3 are of a magnitude generally found with ligands acting monodentately. In both systems, however, the complexity is stronger than in the nickel(II) acetate system,[9] in spite of the lower acidity of the acetic acid. This might be interpreted as owing to some degree of chelating in the systems under investigation. If that is so, the nickel ion should coordinate the ether sulphur somewhat stronger than the ether oxygen since all the stability constants of the nickel (ethylthio)-acetate system are larger than the corresponding ones of the ethoxyacetate system. The effect, however, is much smaller than the one reported [2] for the nickel complexes of oxydiacetate and thiodiacetate ions with log K_1-values of 2.6 and 4.0, respectively.

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