

Estimation of Small Stability Constants in Aqueous Solution. The Nickel(II)–Chloride System

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The weak chloro complex formation in nickel(II) chloride solutions has been studied by several authors. Moore and Kraus,¹ using anion exchange found no evidence for anion complexes even in 12 M HCl, but other authors^{2–4} have shown the existence of both mono- and dichloro complexes in rather concentrated hydrochloric acid solutions. Other workers^{5–9} have made determinations of the 1st stability constant at constant ionic strength and obtained values of K_1 varying from 0.1 to 0.6 l mol⁻¹, whereas Halloff and Vannerberg¹⁰ determined $\beta_2 = K_1K_2$ to be 0.13 l² mol⁻² in 4 M Na(Cl, ClO₄), and found no evidence for NiCl⁺. More trustworthy results are obtained from the spectrophotometric measure-

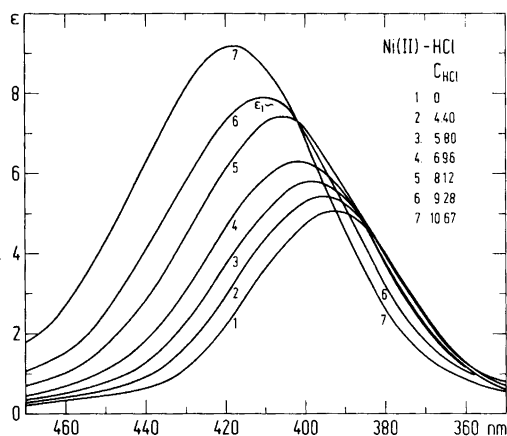


Fig. 1. ϵ, λ absorption spectra of Ni(II)–HCl solutions (2nd visible band) at 25°C.

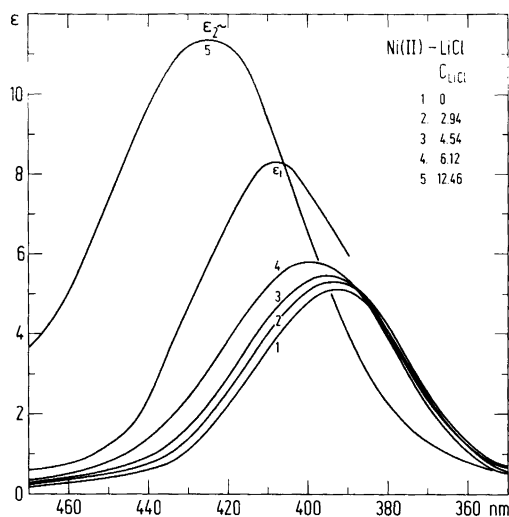


Fig. 2. ϵ, λ absorption spectra of Ni(II)–LiCl solutions (2nd visible band) at 25°C.

ments of Paatero and Hummelstedt.¹¹ These authors corrected their data to zero ionic strength making simplifying assumptions about the activity coefficients and estimated $K_1 \sim 0.05$ l mol⁻¹ and $\beta_2 \sim 0.8 \times 10^{-4}$ l² mol⁻².

In this work the stability constants in concentrated HCl and LiCl solutions have been determined by analysis of the absorption spectra. The necessary activity corrections of the concentration constants were obtained by substituting the chloride concentration with $a_{Cl^-} = \gamma_{\pm}^{(c)} [Cl^-]$ where $\gamma_{\pm}^{(c)}$ are the mean activity coefficients of the

Table 1. Calculated chloride activities in the NiCl₂, HCl solutions at 25°C.

No.	C _{NiCl₂}	C _{HCl}	log γ _{HCl} [±]	γ _{HCl} [±]	a _{Cl⁻}
1	0.0586	0.006			0.10
2	0.0586	4.40	0.40	2.51	11.04
3	0.0586	5.80	0.635	4.315	25.03
4	0.0586	6.96	0.845	7.00	48.7
5	0.0586	8.12	1.08	12.0	97.4
6	0.0586	9.28	1.28	19.0	176
7	0.0586	10.67	1.54	34.6	369

Table 2. Calculated chloride activities in the NiCl₂, LiCl solutions at 25°C.

No.	C _{NiCl₂}	C _{LiCl}	C _{HCl}	log γ _{LiCl} [±]	γ _{LiCl} [±]	a _{Cl⁻}
1	0.0586	0	0.006			0.10
2	0.0586	2.94	0.05	0.10	1.26	3.77
3	0.0586	4.54	0.06	0.35	2.24	0.3
4	0.0586	6.12	0.06	0.65	4.47	27.6
5	0.0586	12.46	0.04	1.62	41.7	521

complex-forming electrolytes converted to a molar basis. This approximation is found to work well in the case of small stability constants where the constant ionic strength principle fails completely.^{12,13} Using this approximation, K_1 is determined to be about 0.01 l mol⁻¹ in HCl, and K_1 about 0.015 l mol⁻¹ in LiCl solutions. β_2 could not be determined directly but was tentatively estimated to be $(0.3-0.8) \times 10^{-4}$ l² mol⁻².

The measurements were made in concentrated HCl and LiCl solutions, monitoring the 2nd visible absorption band, and the spectra of the studied solutions are shown in Figs. 1 and 2. The absorption curves up to 6-7 M chloride concentrations (solutions 1-4) in both Figs. 1 and 2 correspond approximately to those of mixtures of only two species, and are used to calculate the activity-corrected constant K_1 using the earlier derived formula.^{12,13} For three solutions I, II and III with ϵ increasing in the same order, the equation for determining K_1 is given by eqn. (1).*

* An apology is due for a misprint in the formula for determining K_4 in Ref. 12.

$$\frac{(a_{Cl^-})_{III} - (a_{Cl^-})_{II} + \{(a_{Cl^-})_I (a_{Cl^-})_{III} - (a_{Cl^-})_I (a_{Cl^-})_{II}\} K_1}{(a_{Cl^-})_{III} - (a_{Cl^-})_I + \{(a_{Cl^-})_{II} (a_{Cl^-})_{III} - (a_{Cl^-})_I (a_{Cl^-})_{II}\} K_1} = \frac{\epsilon_{III} - \epsilon_{II}}{\epsilon_{III} - \epsilon_I} \quad (1)$$

From the spectra in the hydrochloric acid solutions, K_1 is calculated to be 0.0089 with $\epsilon_4 - \epsilon_3/\epsilon_4 - \epsilon_1 = 0.40 \pm 0.015$, and to be 0.0092 with $\epsilon_4 - \epsilon_2/\epsilon_4 - \epsilon_1 = 0.51 \pm 0.015$. From the spectra in the LiCl solutions, K_1 is calculated to be 0.010 with $\epsilon_4 - \epsilon_3/\epsilon_4 - \epsilon_1 = 0.57 \pm 0.01$, and to be 0.025 with $\epsilon_4 - \epsilon_2/\epsilon_4 - \epsilon_1 = 0.78 \pm 0.01$. Under consideration of the great uncertainty in the calculations, K_1 in the HCl solutions from these results may be taken to be 0.010 ± 0.005 l mol⁻¹, and to be 0.015 ± 0.005 l mol⁻¹ in the LiCl solutions. The chloride activities used in the calculations are shown in Tables 1 and 2. They are converted to a molar basis from the values of γ_{\pm}^m given by Robinson and Stokes.¹⁴

Discussion. The spectrum of the monochloro complex (ϵ_1) is shown in Fig. 2, and is computed from the composition of soln. 4 with $C_{LiCl} = 6.12$ M. The fraction of the monochloro complex, α_1 , is 0.292 calculated with $K_1 = 0.015$ l mol⁻¹, and $\bar{n} = 0.359$ if K_2 tentatively is taken to be 0.005 l mol⁻¹. For soln. 6 with $C_{HCl} = 9.28$ M the ligand number is calculated to be 1.00 with $K_1 = 0.01$ l mol⁻¹ and K_2 tentatively taken to be 0.003 l mol⁻¹. This solution consequently closely reproduces the average spectrum of the monochloro complex. The bond breadth of this spectrum is, as could be expected, somewhat larger than that calculated for ϵ_1 on the basis of the measurements on LiCl solutions. However, it will be noticed that ϵ_{max} and λ_{max} have nearly the same values as those computed for ϵ_1 in Fig. 2.

The red shift of the spectrum of the hexaaqua ion (with λ_{max} at 392.5 nm) to that of the monochloro complex (with λ_{max} at 408-410 nm) is about 16.5 nm. A shift of the same magnitude from the monochloro complex is found for soln. 5 in 12.46 M LiCl, with λ_{max} at 425 nm. It can therefore be concluded that the spectrum of soln. 5 must closely represent the average spectrum of the dichloro complex. The ligand number in this solution with $a_{Cl^-} = 521$ is calculated to be 2.12 when it is tentatively assumed that $K_2 = 1/3 K_1$ and $K_3 = 1/9 K_1$.

The spectra discussed were all measured for the 2nd visible absorption band. The spectra of three solutions measured for the 1st visible band

SHORT COMMUNICATION

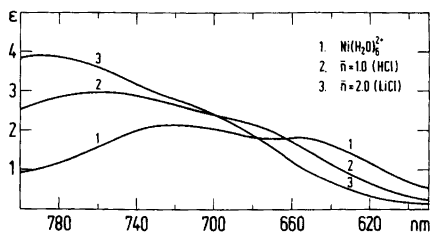


Fig. 3. ϵ, λ absorption spectra of Ni(II)-chloride solutions (1st visible band) at 25°C. 1. $C_{\text{NiCl}_2} = 0.0586$, 2. $C_{\text{HCl}} = 9.28$, 3. $C_{\text{LiCl}} = 12.46$ M.

are shown in Fig. 3, namely those of the hexa-aqua ion, of soln. 6 in Fig. 1 with $\bar{n} = 1.00$, and of soln. 5 in Fig. 2.

Experimental. The chemicals used were of analytical grade. Stock solutions of $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$ *p.a.* were analysed by electrolysis. The stock solutions of 37% HCl and nearly saturated LiCl were analysed by acid-base and Volhard titrations. The absorption spectra were measured with a Cary 118 spectrophotometer thermostatted to 25°C.

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