Short Communication

Estimation of Small Stability Constants in Aqueous Solution. The Fourth Consecutive Stability Constant in the Nickel(II)-Thiocyanate System

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Many authors have studied the Ni(II)-thiocyanate system in aqueous solution, and a selected compilation of reported values for this system is given in Table 1. Most authors have determined only the first stability constant. However, good values for the first three consecutive constants were determined in 1 M Na(SCN, ClO_4) by Fronæus[1] (by cation-exchange) and by Kullberg[2] (by calorimetric titrations). Values for all four consecutive constants are given by Tribalat[3] and also by Landers *et al.*,[8] but Tribalat's value for the fourth consecutive constant seems suspicious, while the values for the activity constants given by Landers *et al.* cannot be trusted. On the other hand, the values for the 1st activity constants given by three independent workers[5–7] appear to be very reliable. This note describes the estimation of the fourth consecutive activity constant by spectrophotometric measurements, giving the value 0.12 ± 0.04 l mol^{-1} in concentrated NaSCN solutions. This constant is so small that it cannot be estimated by the usual procedure by working at constant ionic strength in a mixed solution with an inert electrolyte. The latter method fails completely when the constants are smaller than ~ 1 l mol^{-1}, as discussed in a recent paper.[9] However, good results are obtained by estimating small equilibrium constants at high concentrations of the particular electrolyte using c $\gamma_{\pm}^{c}$ as a measure for the activity of the complex forming anion.[10,11]

Table 1. Comparison of reported values of stability constants K_n (l mol^{-1}) and enthalpy changes (kJ $mole^{-1}$) of the nickel(II)-thiocyanate system.

Ref.[a]	Method	t°C	I	K_1	K_2	K_3	K_4	$-\Delta H_1^0$	$-\Delta H_2^0$
53 F[1]	cix	20	1.0	15.0±0.5	2.94	1.48	–	–	–
74 K[2]	cal	25	1.0	13.4±0.7	2.76	0.49	–	12.0	8.9
64 T[3]	dis	20	1.5	13.8	4.1	0.89	2.2		
62 F[4]	IR		3.0	15.0[b]	–	–	–		
62 W[5]	sp	25	→ 0	57	–	–	–		
67 N[6]	cal	25	→ 0	58	–	–	–	9.4	
74 D[7]	kin	20	→ 0	67	–	–	–		
71 L[8]	aix		→ 0	166	1.62	1.55	0.34		
88 Bj	sp	25	→ 0	–	–	–	0.12±0.04		

[a]Ref. gives year of publication and first letter of author's name. [b]K_1^{in} = 12±2, K_1^{out} = 3±2.

Experimental

The chemicals used were of analytical grade. The stock solution of $NiCl_2 \cdot 6H_2O$ was analysed by electrolysis. The stock solutions of KSCN and NaSCN were analysed by silver nitrate titration. The absorption spectra were recorded with a Cary 118 spectrophotometer thermostatted to 25 °C.

The spectrophotometric measurements were first performed in concentrated KSCN solutions, and the derived ε,λ curves are plotted in the lower part of Fig. 1. The behaviour of the curves rather closely resembles that for an isosbestic mixture of only two species in the concentration range in which the tricyanato complex is converted to the tetracyanato complex. However, as the mean activity coefficients of KSCN are only determined up to 4 M,[12] these data cannot be used to calculate the stability constant. For NaSCN the activity coefficients are known for concentrations up to saturation,[13] and K_4 could therefore be calculated by use of the absorption curves shown in the upper part of Fig. 1.

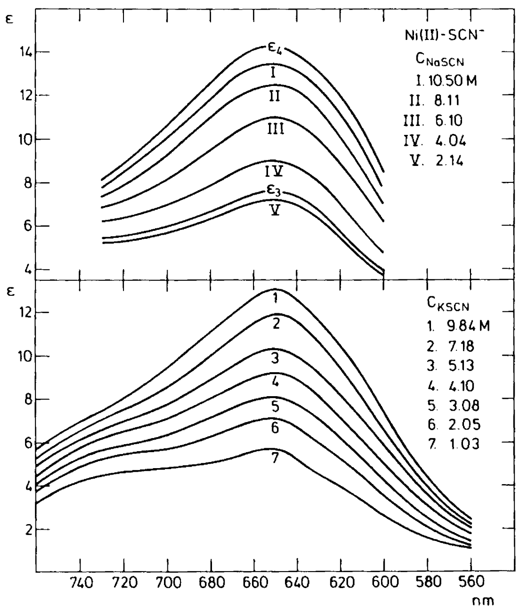

Fig. 1. ε,λ-absorption spectra of Ni(II)-thiocyanate solutions at high concentrations of KSCN and NaSCN. The Ni(II) concentrations were in the range 0.02–0.04 M. In sols. I–V the Ni(II) concentration was 0.01955 M.

Table 2. Estimations of K_4 by use of three absorption curves.

Fraction	Calc. for K_4
$\frac{\varepsilon_I - \varepsilon_{II}}{\varepsilon_I - \varepsilon_{III}} = 0.385 \pm 0.020$	0.14±0.04
$\frac{\varepsilon_I - \varepsilon_{III}}{\varepsilon_I - \varepsilon_{IV}} = 0.565 \pm 0.020$	0.10±0.02
$\frac{\varepsilon_{II} - \varepsilon_{III}}{\varepsilon_{II} - \varepsilon_{IV}} = 0.435 \pm 0.025$	0.11±0.03
Av.	0.12±0.04

Table 3. Calculated activities of NaSCN on molar basis.

Sol.	c_{NaSCN}	γ^c_{NaSCN}	a_{SCN^-}
I	10.50	5.76	60.5
II	8.11	3.45	28.0
III	6.10	2.08	12.7
IV	4.04	1.24	5.02
V	2.14	0.82	1.76

The stability constant was estimated by use of the formula[10,11] derived earlier, from which the constant can be calculated from three absorption curves which satisfy the condition of being isosbestic. The curves I–IV in the range from 4 to 10 M were used for the calculations. The fractions of the molar absorbance differences are combined as shown in Table 2. Their average values are estimated in the wavelength range from 700 to 620 nm, and used together with the ligand activities estimated in Table 3 to calculate K_4.

Discussion

The mean value of 0.12±0.04 for the calculated activity constant can be compared directly with the values of $K_1 \sim 60$ estimated at ionic strength zero in Table 1. Table 4 gives the distribution of the complexes in solutions. I–V calculated when the value of K_4 is tentatively combined with Kullberg's[2] "best values" for K_1, K_2 and K_3 in 1 M NaSCN. The spectra of the tetracyanato (ε_4) and of the tricyanato complex (ε_3) shown in Fig. 1 are estimated using the ligand numbers of solutions I (3.875) and IV (3.21) in Table 4. The ligand number in solution V is calculated to be

Table 4. Degrees of formation of the different complexes calc. with: K_1 = 13.8, K_2 = 3.8, K_3 = 1.05, K_4 = 0.12.

Sol.	α_0	α_1	α_2	α_3	α_4	$\bar{n}$
I	1.3×10^{-8}	1.1×10^{-5}	0.0019	0.121	0.877	3.875
II	2.6×10^{-7}	1.0×10^{-4}	0.0077	0.227	0.765	3.757
III	4.7×10^{-6}	8.2×10^{-4}	0.029	0.384	0.586	3.555
IV	1.1×10^{-4}	0.0075	0.105	0.554	0.334	3.213
V	0.0025	0.060	0.289	0.536	0.113	2.697

2.70. However, if the activity constants $K_1 \sim 60$ and $K_4 \sim 0.12$ are combined with Fronæus' values for K_2 and K_3 in 1 M NaSCN (converted to 25 °C),[2] $\bar{n}$ is calculated to be 2.81 in solution V. This is probably more correct as the salt sensitivity of K_1 is higher than for K_2 and K_3, and it is also in better agreement with the estimated values for the spectrum of the trithiocyanato complex.

References

1. Fronæus, S. *Acta Chem. Scand. 7* (1953) 21.
2. Kullberg, L. *Acta Chem. Scand., Ser. A 28* (1974) 829.
3. Tribalat, S. and Caldero, J. M. *C. R. Acad. Sci. 258* (1964) 2828.
4. Fronæus, S. and Larsson, R. *Acta Chem. Scand. 16* (1962) 1433.
5. Williams, T. J. *J. Inorg. Nucl. Chem. 24* (1962) 1215.
6. Nancollas, G. H. and Torrance, K. *Inorg. Chem. 6* (1967) 1567.
7. Dickert, F., Hoffmann, H. and Janjec, T. *Ber. Bunsenges. Phys. Chem. 78* (1974) 712.
8. Landers, L. and Cummiskey, C. J. *J. Inorg. Nucl. Chem. 33* (1971) 4239.
9. Bjerrum, J. *Coord. Chem. Rev.* (1988). *In press.*
10. Bjerrum, J. and Lukeš, I. *Acta Chem. Scand., Ser. A 40* (1986) 31.
11. Bjerrum, J. *Acta Chem. Scand., Ser. A 42* (1988). *In press.*
12. Robinson, R. A. and Stokes, R. H. *Electrolyte Solutions,* Butterworth, London 1959, p. 494.
13. Miller, M. L. and Sheridan, C. L. *J. Phys. Chem. 60* (1956) 184.

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