Short Communication

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

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In 1936 Job[1] studied spectrophotometrically the nickel(II)–bromide complex formation in concentrated hydrogen bromide solutions and found values for $\beta_2 \approx 10^{-3.24}$ l^2 mol^{-2} and for $K_3K_4 \approx 10^{-4.88}$ l^2 mol^{-2} under the assumption that $NiBr_2$ and $NiBr_4^{2-}$ were the only complexes. It is noteworthy that Job in his calculations applied semi-thermodynamic stability constants in which the bromide concentrations are substituted by $\gamma_{\pm}[Br^-]$. Retajczyk and Hune[2] studied spectrophotometrically the complex formation in 8.5–11.7 M LiBr solutions and estimated the semi-thermodynamic stability constant K_2 to have the value $10^{-4.25}$ l mol^{-1}. Other authors[3–6] have studied the complex formation at high ionic strength held constant with sodium perchlorate and obtained uncertain values for the first stability constant. This method using bromide–perchlorate mixtures works well if the stability constants are not too small ($K_n > 1$ l mol^{-1}), but fails in the case of very weak complex formation. This has been discussed recently.[7]

In this paper the first stability constant is estimated in LiBr solutions by analysis of the absorption spectra of solutions which only contain two species. The semi-thermodynamic mass action law with $\gamma^c_{\pm}[Br^-]$ substituted for the bromide ion concentration was used. K_1 was calculated to be $10^{-2.37}$, which is somewhat smaller than the value found for the corresponding constant ($10^{-1.82}$) in the Ni(II)–LiCl system.[8] The red shift of the main absorption band on uptake of the first bromide ion was found to be 17 nm, which may be compared to the shift of 16 nm in the chloride system.[8] It is estimated from the red shifts of the measured spectra that a yellow dibromonickel(II) complex is dominating in 10–11 M LiBr.

Experimental

The chemicals used were of analytical grade. The nearly saturated stock solution of LiBr was analysed by Volhard titration. The small Ni(II) concentration was prepared from a stock solution of $NiCl_2$. Nickel chloride was used instead of $NiBr_2$ without any influence on the precision of the measurements. The absorption spectra were measured with a Cary 118 spectrophotometer thermostatted to 25 °C.

Measurements

The spectra of the Ni(II)–LiBr solutions measured in the second visible band between 460 and 360 nm are shown in Fig. 1. The absorption curves up to 7.66 M LiBr (solutions I–V) closely resemble those of mixtures of only two species and are used to calculate the activity-corrected first stability constant K_1. Three solutions a, b and c with ε increasing in the same order are necessary for this purpose.

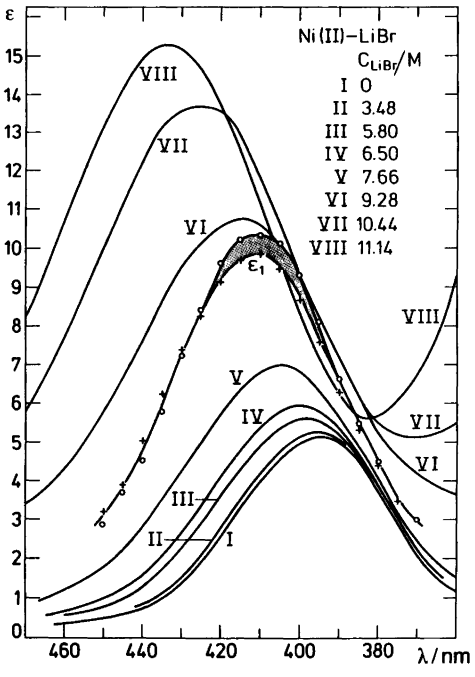

Fig. 1. ε vs. λ absorption spectra of Ni(II)–LiBr solutions in the second band at 25°C. The shadowed area indicates the uncertainty in the spectrum of the monobromonickel(II) complex.

The required ligand salt activities $a_{\pm}$ and the measured molar absorbances are correlated by the following equation.[8]

$$\frac{(a_{\pm})_c - (a_{\pm})_b + [(a_{\pm})_a(a_{\pm})_c - (a_{\pm})_a(a_{\pm})_b]K_1}{(a_{\pm})_c - (a_{\pm})_a + [(a_{\pm})_b(a_{\pm})_c - (a_{\pm})_a(a_{\pm})_b]K_1} = \frac{\varepsilon_c - \varepsilon_b}{\varepsilon_c - \varepsilon_a}$$

The LiBr activities ($a_{\pm} = \gamma^c_{\pm}[Br^-]$) in the studied solutions as shown in Table 1 are calculated from the isopiestic measurements of Robinson and Stokes.[9] The results of the calculations of K_1 by use of the solutions I, III, IV and V are shown in Table 2. The ratios $(\varepsilon_c - \varepsilon_b)/(\varepsilon_c - \varepsilon_a)$ of the molar absorbance differences shown in the table are average values estimated at 5 nm intervals in the wavelength range from 395 to 435 nm. The calculated values of the stability constant are shown in the last column of Table 2. Using the average value $K_1 = 0.0043 \pm 0.0007$ l mol^{-1}, the ligand numbers in solutions II, III and IV are calculated to be $\bar{n} =$ 0.03, 0.14 and 0.22, respectively. The spectrum of the monobromo complex (ε_1) in Fig. 1 is calculated by use of the absorption spectrum of solution IV with $\bar{n} = 0.22$ (the upper curve with open circles) as well as by use of solution V with $\bar{n}$ calculated to be 0.48 (the lower curve for ε_1 with crosses). The data for the maximum of the monobromo spectrum $\varepsilon_{max} \approx 10$ at 411 nm are compared in Table 3 with the corresponding data for the studied equilibrium solutions. The red shift of λ_{max} from the hexa-aqua ion to the monobromo complex is found to be 17 nm. It is a common rule[10] that the shift of the absorption band is almost the same for each step in a normal complex system. It is therefore reasonable to assume that $\Delta\lambda$ is roughly proportional to $\bar{n}$, and the values given for $\bar{n}_{\Delta}$ in Table 3 are calculated under this assumption. The values are seen to agree fairly well with those $\bar{n}_{calc}$ in the last column of the table. In order to calculate $\bar{n}$ for the solutions V–VIII it is necessary to make some assumptions about the succeeding stability constants K_2 and K_3. The $\bar{n}$-values in Table 3 are calculated under the assumption that $K_2 = \frac{1}{4} K_1$ and $k_3 = \frac{1}{16} K_1$. The uncertainties in these values are estimated under the assumption that K_2 can vary between $\frac{1}{3} K_1$ and $\frac{1}{5} K_1$, and K_3 between $\frac{1}{9} K_1$ and $\frac{1}{25} K_1$.

Table 1. Activity of LiBr on molar basis in the studied Ni(II)–bromide solutions.[9]

No.	$C_{Ni(II)}$/M	C_{LiBr}/M	$\gamma^c_{\pm}$	$\gamma^c_{\pm}[Br^-]$	a_{H_2O}
I	0.0587	0	~0.5	~0.06	1
II	0.0587	3.48	1.995	6.94	0.83
III	0.0587	5.80	6.03	35.0	0.60
IV	0.0587	6.50	8.91	57.9	0.51
V	0.0391	7.66	19.5	149.3	0.37
VI	0.0391	9.28	70.8	657	0.224
VII	0.0391	10.44	158.5	1655	0.132
VIII	0.0391	11.14	251	2796	0.100

Table 2. Estimations of the first stability constant in the Ni(II)–bromide system by analysis of isosbestic absorption spectra.

Solutions used	$\frac{\varepsilon_c - \varepsilon_b}{\varepsilon_c - \varepsilon_a}$	$K_1 = \frac{[NiBr^+]}{[Ni^{2+}][Br^-]\gamma^c_{\pm}}$
I, III, V	0.650±0.008	0.0051±0.0005
I, IV, V	0.515±0.012	0.0033±0.0005
I, III, IV	0.344±0.010	0.0044±0.0009
		Av. 0.0043±0.0007

Table 3. ε and λ data for the maxima and values of ligand numbers ($\bar{n}_{\Delta}$) estimated from the red shift ($\Delta\lambda$) of the absorption curves.

No.	ε_{max}	λ_{max}	$\Delta\lambda_{max}$	$\bar{n}_{\Delta}$	$\bar{n}^a_{calc}$
I	5.15	394	0	0	0
II	5.25	394.5	0.5	~0.03	0.029
III	5.6	399	3	~0.18	0.14
IV	5.95	397	5	~0.29	0.22
V	7.0	404	10	~0.58	0.48±0.01
ε_1	10.2	411	17	1	1
VI	10.75	415	21	~1.24	1.27±0.11
VII	13.7	426	32	~1.88	1.87±0.16
VIII	15.3	433	39	~2.29	2.17±0.21

[a]Calculated with $K_1 = 0.0043$ l mol^{-1}, $K_2 = \frac{1}{4} K_1$, $K_3 = \frac{1}{16} K_1$. The uncertainties in $\bar{n}_{calc}$ are estimated under the assumption that K_2 can vary between $\frac{1}{3} K_1$ and $\frac{1}{5} K_1$, and K_3 between $\frac{1}{9} K_1$ and $\frac{1}{25} K_1$.

Discussion

The semi-thermodynamic mass action expression given by eqn. (1), where $a_L = [L]\gamma^c_{\pm}$, has been used in several papers by the author[8,11,12] to estimate small stability constants in aqueous systems of complexes formed from the metal ion in the presence of only the complex-forming salt in high concentration.

$$K_n = [M\,L_n]/[M\,L_{n-1}]\,a_L \qquad (1)$$

The basis for using this mass action law is discussed in Ref. 7. The binding of a ligand ion in aqueous solution is accompanied by displacement of a water molecule. One could therefore expect that eqn. (2), where a_{H_2O} is the water activity, would give better approximations of the thermodynamic constants.

$$K_n = [M\,L_n]\,a_{H_2O}/[M\,L_{n-1}]\,a_L \qquad (2)$$

However, one cannot be sure that this always is the case. In the copper(II) chloride system[12] it has been shown that calculation of K_4 in concentrated chloride solutions by use of eqn. (1) gave nearly the same results as those calculated with an activity function adjusted to the measurements. For the robust chromium(III) chloride system[10] using HPLC

measurements the ratios between the concentrations of succeeding complexes in equilibrium solutions have been determined over large ranges of LiCl concentrations. Since it was found for this chromium system that eqn. (2) gives decreasing values of K_1 and K_2 with an increase in the LiCl concentration, while the use of eqn. (1) gives increasing values, so that neither of these treatments is exact.

It is eqn. (1) which is used in the present paper and also in the previous paper on nickel(II) chloride.[8] The value of K_1 calculated by use of eqn. (2), which on average is determined to be 0.0053 l mol^{-1}, is not appreciably different from that calculated by use of eqn. (1), 0.0043 l mol^{-1}. However, the much larger activity correction caused by the decreasing water activity (cf. Table 1) in the first results in higher $\bar{n}$-values, with the consequence that the calculated spectrum of the monobromo complex is situated at a lower wavelength (407 nm) and with a lower value for $\varepsilon_{max} \approx 8$ than the monobromo spectrum calculated by use of eqn. (1) and situated at 411 nm with $\varepsilon_{max} \approx 10$, cf. Fig. 1. A closer discussion of the problems by using semithermodynamic mass-action constants will be made in a forthcoming paper dealing with complex formation in the chromium(III) bromide system.

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