

## A Potentiometric Study on the Complex Equilibria between Uranyl Ions and 3-Hydroxy-5,7-disulfo-2-naphthoic Acid

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In the preceding papers the complex equilibria between  $\text{Cu}^{2+}$ ,  $\text{Be}^{2+}$  or  $\text{Al}^{3+}$  ions and 3-hydroxy-5,7-disulfo-2-naphthoic acid have been investigated.<sup>1-6</sup> In addition to the binary systems, the formation of ternary complex species of copper and beryllium ions with 3-hydroxy-5,7-disulfo-2-naphthoic acid as one of the ligands has also been studied.<sup>1-5</sup> In the binary systems the data clearly indicated the formation of ML and  $\text{ML}_2$  complexes ( $\text{M} = \text{Cu}^{2+}$ ,  $\text{Be}^{2+}$  or  $\text{Al}^{3+}$  ion, and L = unprotonated 3-hydroxy-5,7-disulfo-2-naphthoic acid anion), and in the case of the ternary systems the formation of mixed ligand complex compounds with composition MXY ( $\text{M} = \text{Cu}^{2+}$  or  $\text{Be}^{2+}$  ion, X = 3-hydroxy-5,7-disulfo-2-naphthoic acid, and Y = 3,5-disulfosalicylic, 1-hydroxy-4,7-disulfo-2-naphthoic, catechol-3,5-disulfonic or chromotropic acid).

The present investigation was carried out to determine the species formed in the binary systems of uranyl ions and 3-hydroxy-5,7-disulfo-2-naphthoic acid. This study was carried out in the same conditions [ $t = 25^\circ\text{C}$  and  $I = 0.5$  ( $\text{NaClO}_4$ )] as were the earlier investigations of 3-hydroxy-5,7-disulfo-2-naphthoic acid.

**Experimental. Reagents.** The preparation and purification of the disodium salt of 3-hydroxy-5,7-disulfo-2-naphthoic acid has been described earlier.<sup>1,4</sup>

Stock solutions of uranyl ions were prepared from the corresponding nitrate (E. Merck AG, 99.9%). The concentrations of these solutions were determined by potentiometric neutralization titrations, after passage through a cation exchanger.

**Apparatus.** The potentiometric titrations were carried out automatically with a Radiometer digital titration system DTS 633, consisting of an autoburette ABU 13, a pH meter PHM 64, a digital titrator TTT 61, and an equal increment accessory constructed in this laboratory.

The other details of the apparatus are described in the earlier papers.<sup>1-4</sup>

**Methods.** Two different types of titration were carried out for resolving the stability constants:

(a) During the titrations of the first kind the total concentrations of uranium  $C_M$ , and 3-hydroxy-5,7-

disulfo-2-naphthoic acid,  $C_L$ , were kept constant. The ratio  $C_L:C_M$  was varied systematically between 1 and 7 in the separate titrations. The free hydrogen ion concentration,  $[\text{H}^+]$ , was decreased by adding sodium hydroxide. The reversibility of the equilibria system was tested by also reversing some of the titrations by adding standardized perchloric acid into the solution to be titrated.

(b) In the titrations of the second kind the total concentration of protons,  $C_H$ , and 3-hydroxy-5,7-disulfo-2-naphthoic acid was kept constant. The ratio  $C_L:C_M$  was varied during the measurements by adding a standardized solution of uranyl ions. The readings of the titration steps were taken in the range where the ratio  $C_L:C_M$  was between 10 and 0.5.

Precipitates appeared in neutral and alkaline solutions, and hence the available  $-\log[\text{H}^+]$  range was restricted to an upper limit of 6-7.

Because of the poor solubility of 3-hydroxy-5,7-disulfo-2-naphthoic acid, the total concentrations of uranium and 3-hydroxy-5,7-disulfo-2-naphthoic acid were varied within the limits of 0.001 and 0.010 M.

A constant ionic medium of 0.5 M  $\text{NaClO}_4$  was used in order to avoid the changes in the activity coefficient. The buffer solutions, the solutions to be titrated and the titrant solutions were all 0.5 M with regard to  $\text{NaClO}_4$ .

The calibration of the glass electrode and the determination of the liquid junction potential,  $E_j$ , were performed as described earlier.<sup>4</sup>

**Calculations.** The values 10.92 and 2.14 were used for the logarithms of the first and second protonation constants of the ligand anion, respectively.<sup>1</sup>

The experimental values of the  $\bar{n}$  function were calculated by means of the following equation:<sup>7</sup>

$$\bar{n}(\text{exp}) = \{C_L - [C_H - ([\text{H}^+] - K_w[\text{H}^+]^{-1})]/\bar{n}_H\}/C_M \quad (1)$$

where  $K_w$  is the stoichiometric ionic product of water,  $\bar{n}_H$  the average number of protons bound to ligand anion ( $\bar{n}_H = \sum_{i=1}^2 i\beta_i[\text{H}^+]^i / \sum_{i=0}^2 \beta_i[\text{H}^+]^i$ ),  $\beta_i$  is the overall protonation constant of the acid  $\text{H}_i\text{L}$ ).

The values of the constants were calculated as overall stability constants  $\beta_{qpr}$  with the programmes SCOGS<sup>8</sup> and MINIQUAD<sup>9</sup> on a Univac 1100/20 computer.

The overall stability constant of a general complex  $\text{M}_q\text{H}_p\text{L}_r$  is defined by

$$\beta_{qpr} = [\text{M}_q\text{H}_p\text{L}_r]/[\text{M}]^q[\text{H}]^p[\text{L}]^r \quad (2)$$

where the square brackets indicate the concentrations of the free metal, hydrogen and ligand ions.

Table 1. The stability constants of uranyl, beryllium, copper and aluminum complexes of 3-hydroxy-5,7-disulfo-2-naphthoic acid at  $I=0.5$  ( $\text{NaClO}_4$ ) and  $25^\circ\text{C}$ .  $\{k_n=K(\text{ML}_{n-1}+\text{L}=\text{ML}_n)$  and  $R=[\sum\phi_i^{\text{obs}}-\phi_i^{\text{calc}}]^2/\sum(\phi_i^{\text{obs}})^2\}^{1/2}$ . The values in parentheses are the standard deviations.

M	$\log \beta_{101}$	$\log \beta_{102}$	$\log k_2$	$\log (\beta_1/k_2)$	R	$\chi^2$	Refs.
$\text{UO}_2^{2+}$ <sup>a</sup>	9.809(3)	17.398(5)	7.59	2.2	0.0005	6.5	This work
$\text{Be}^{2+}$	10.18	18.17	7.99	2.2			1, 4
$\text{Cu}^{2+}$	8.18	14.11	5.93	2.3			1, 4
$\text{Al}^{3+}$	10.81	19.26	8.45	2.4			6

<sup>a</sup>No. of titrations: 11; No. of data points: 385.

The programme MINQUAD calculates, along with the stability constants, their standard deviations, an agreement index  $R$  and a  $\chi^2$  statistics.<sup>9,10</sup>

**Results and discussion.** The data were visualized by presenting experimental values of  $\bar{n}$  versus  $-\log [\text{L}]$  (Fig. 1). It can be seen from this plot that the function  $\bar{n}(-\log [\text{L}])$  seems to be independent of  $C_L$ ,  $C_M$  and  $C_H$ , thus indicating the formation of stepwise metal complexes  $\text{UO}_2\text{L}_r^{-(4r-2)}$ . The highest experimental value of  $\bar{n}$  is about 1.6, which means that at least two successive complex compounds are formed in the conditions studied. Because of precipitations, the measurements were only possible in the acidic pH region, and that is why the experimental  $\bar{n}$  values are all under 1.6.

Computations with the programmes SCOGS and MINQUAD showed that the data were well explicable with two complex compounds:  $\text{UO}_2\text{L}_2^-$  and  $\text{UO}_2\text{L}_2^{6-}$ . The best stability constants with the corresponding standard deviations, and the values of  $R$  and  $\chi^2$ , are given in Table 1. For the sake of comparison, the table also shows the stability constants of the corresponding complexes of copper(II), beryllium(II) and aluminum(III) ions. According to the values of the standard deviations,  $R$  and  $\chi^2$ , the model of two parameters,  $\beta_{101}$  and  $\beta_{102}$ , must be considered a good approximation. At a 95% confidence level the value of  $\chi^2$  should be less than 12.6 ( $\chi^2$  is the measure of the conformity to normal distribution of the residuals  $\phi_i^{\text{obs}}-\phi_i^{\text{calc}}$ ).<sup>11</sup> The value of  $R$  should be as small as possible.

The complex equilibria between  $\text{UO}_2^{2+}$ ,  $\text{Be}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Al}^{3+}$  ions with 3-hydroxy-5,7-disulfo-2-naphthoic acid at  $I=0.5$  ( $\text{NaClO}_4$ ) and  $25^\circ\text{C}$  in the acidic pH region are similar: two successive complex compounds,  $\text{ML}$  and  $\text{ML}_2$ , are formed and the data give no evidence of protonated, hydrolyzed or polynuclear complex species. The stability of the complexes of 3-hydroxy-5,7-disulfo-2-naphthoic acid decreases in the order  $\text{Al}$ ,  $\text{Be}$ ,  $\text{UO}_2$ ,  $\text{Cu}$ . Also, the ratio  $\log(\beta_1/k_2)$  is equal for all the metal systems, indicating that addition of the second

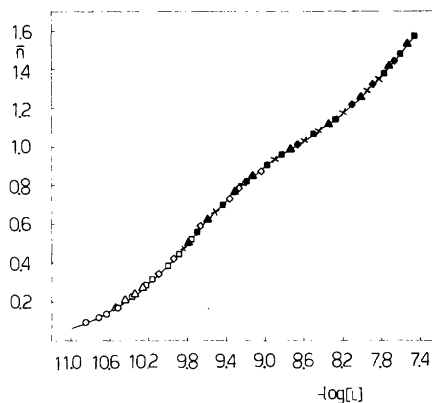


Fig. 1. Experimental values of  $\bar{n}$  versus  $-\log [\text{L}]$  calculated from a few different titrations.  $\square$ ,  $C_H=5.90 \times 10^{-3}$  M,  $C_L=3.95 \times 10^{-3}$  M;  $\triangle$ ,  $C_H=4.90 \times 10^{-3}$  M,  $C_L=3.95 \times 10^{-3}$  M;  $\circ$ ,  $C_H=3.90 \times 10^{-3}$  M,  $C_L=3.95 \times 10^{-3}$  M;  $\diamond$ ,  $C_H=2.90 \times 10^{-3}$  M,  $C_L=3.95 \times 10^{-3}$  M. Titrant in the first four titrations = 0.1 M  $\text{UO}_2(\text{NO}_3)_2$  solution;  $\times$ ,  $C_M=2.00 \times 10^{-3}$  M,  $C_L=5.93 \times 10^{-3}$  M;  $\blacktriangle$ ,  $C_M=1.00 \times 10^{-3}$  M,  $C_L=4.94 \times 10^{-3}$  M;  $\blacksquare$ ,  $C_M=1.00 \times 10^{-3}$  M,  $C_L=7.90 \times 10^{-3}$  M;  $\blacklozenge$ ,  $C_M=3.00 \times 10^{-3}$  M,  $C_L=7.90 \times 10^{-3}$  M, titrant in the last four titrations = 0.1 M NaOH solution.

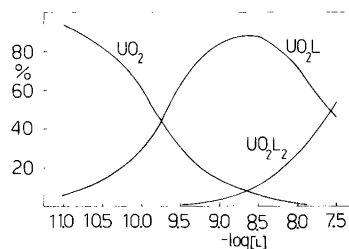


Fig. 2. Distribution of the different metal species as a function of  $-\log [\text{L}]$ .

ligand molecule to the monocomplexes is equally hindered in every case.

The distribution of the different uranyl species in the  $-\log [L]$  region studied is presented in Fig. 2.

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Received March 29, 1978.