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in the NaCl/NaClO₄ System

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Spectrophotometric Investigation of U(VI) Chloride Complexation in the NaCl/NaClO₄ System

February 1, 1999

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SUMMARY

The option of a nuclear waste disposal in deep salt formations such as Gorleben in Germany, and the WIPP (Waste Isolation Pilot Plant) in Southeastern New Mexico, USA has generated, over the last past ten years, interests in thermodynamic data of radioactive trace elements in concentrated electrolyte solutions. Furthermore, post closure radioactive release scenarios from geologic salt formation, such as the WIPP include hydrologic transport of radionuclides through a chloride saturated aquifer. Consequently, the understanding of actinide solution chemistry in brines is essential for modeling requiring accurate knowledge of the interaction between AnO_2^{2+} and chloride ions. Our goal is to develop models capable of predicting their behavior in natural multicomponent brines of high concentration. Complexation constants of two U(VI) chloride species, UO_2Cl^+ and UO_2Cl_2^0 , have been intensively studied for about 40 years using different methods. However, large uncertainties reflect the general difficulty in determining accurate stability constants of weak complexes. In order to model the behavior of U(VI) in brines, we studied the formation of its chloride complexes by UV-Vis spectroscopy as a function of the NaCl concentration at 25°C. Two sets of experiments were performed: (1) at constant ionic strength by varying the concentration ratio of NaCl and NaClO_4 , and (2) at different ionic strengths in pure NaCl solutions. Deconvolution resulted in single component absorption spectra for UO_2Cl^+ and UO_2Cl_2^0 . The apparent stability constants of UO_2Cl^+ and UO_2Cl_2^0 were determined at different ionic strengths. The apparent stability constants of UO_2Cl^+ are found to be $\log \beta_1 = -0.339 \pm 0.01$ at $I=0.45 \text{ mol/kgH}_2\text{O}$, $\log \beta_1 = -0.449 \pm 0.007$ at $I=0.78 \text{ mol/kgH}_2\text{O}$, $\log \beta_1 = -0.419 \pm 0.012$ at $I=1.05 \text{ mol/kgH}_2\text{O}$, $\log \beta_1 = -0.301 \pm 0.023$ at $I = 2.48 \text{ mol/kg H}_2\text{O}$, $\log \beta_1 = -0.154 \pm 0.005$ at $I = 3.71 \text{ mol/kg H}_2\text{O}$, and $\log \beta_1 = 0.0321 \pm 0.004$ at $I = 4.98 \text{ mol/kg H}_2\text{O}$. The apparent stability constants of UO_2Cl_2^0 are found to be $\log \beta_2 = -1.526 \pm 0.087$ at $I=2.48 \text{ mol/kgH}_2\text{O}$, and $\log \beta_2 = -1.214 \pm 0.025$ at $I=4.98 \text{ mol/kgH}_2\text{O}$. The experimental data are used to parameterize using the SIT (Specific Ion Interaction Theory) approach.

I. INTRODUCTION

The option of a nuclear waste repository in a deep salt formation attracts the attention of the international environmental community. In the US, as well as in Germany, we began a systematic investigation of actinide solution chemistry in brines in order to model their behavior in natural multicomponent brines of high concentration [1-5]. The US's first geologic repository for radioactive waste is being excavated in southeastern New Mexico at the WIPP. Post closure radioactive release scenarios from the WIPP often involve hydrologic transport of radionuclides through the overlying Rustler Formation, in the Culebra Dolomite Member, a NaCl type water. Consequently, the knowledge of uranium solution chemistry in brines is important in understanding its chemical behavior and requires additional comprehension concerning the interaction between UO_2^{2+} and chloride ions. Furthermore, thermodynamic data pertinent to the interaction of actinides with groundwater are critical input to modeling programs for nuclear waste disposal. Complexation constants of U(VI) chloride species have been intensively studied through different methods. Most data have been obtained applying techniques like cation exchange [6-8], potentiometry [9], spectrophotometry [10-15]. The large part of the scattering of experimental data incite us to report new data concerning the dioxouranium (VI) chloride complexes formation in NaCl solution.

II. EXPERIMENTS AT CONSTANT IONIC STRENGTH

II.1. Experimental

The NaCl and NaClO_4 were purchased from Aldrich Chemicals suprapure (99.99%) and were used without further purification. The source of uranium was depleted Nuclear Grade Uranium(VI) nitrate 6-hydrate, dissolved in de-ionized water to a concentration of 0.15 mol/L. The stock solution was made by dissolving 1.8856 g of $\text{UO}_2(\text{NO}_3)_6 \cdot 6\text{H}_2\text{O}$ in 24.2841 g of H_2O . The uranium total concentration was 0.15467 mol/L.

A 0.01 M HClO_4 stock solution was prepared, which is a sufficient acidic medium to prevent the hydrolysis of uranium. U(VI) concentration was determined by UV-Vis spectroscopy using Beer-Lambert's law. The solution was stirred constantly, in order to

have a homogeneous solution. The absorption spectra were taken 2 days later, after reaching the equilibrium.

II.1.1 Experimental - Ionic strength $I = 0.45 \text{ mol/kg H}_2\text{O}$

Experimental solutions were prepared from the stock solution described previously (§ II.1) using $\text{NaCl}/\text{NaClO}_4$ to maintain a constant ionic strength of $0.45 \text{ mol/kg H}_2\text{O}$. Samples were prepared by adding in a 10 mL scintillation vial, to a 0.5 mL of the $0.15 \text{ M UO}_2(\text{NO}_3).6 \text{ H}_2\text{O}$ stock solution, a suitable amount of the solid salts NaCl and NaClO_4 to obtain the desired ionic strength for each series, and 5 mL of 0.01 M HClO_4 . The exact amount of NaCl , NaClO_4 , the stock solutions of $0.15 \text{ M UO}_2(\text{NO}_3).6 \text{ H}_2\text{O}$, and 0.01 M HClO_4 are displayed in table 1.

Table 1. Experimental conditions description at $I = 0.45 \text{ mol/kg H}_2\text{O}$

Sample	Mass NaClO_4 (g)	Mass NaCl (g)	Mass UO_2NO_3 (g)	Mass of 0.01M HClO_4 (g)	$[\text{NaClO}_4]$ (mol/kg H_2O)	$[\text{NaCl}]$ (mol/kg H_2O)	$[\text{UO}_2^{2+}]$ (mol/kg H_2O)	Ionic Strength
0.45-A	0.4505	0	0.4946	5.0118	0.4534	0	0.0139	0.4534
0.45-D	0.3626	0.0292	0.5012	5.0033	0.3650	0.0908	0.0141	0.4558
0.45-B	0.2741	0.0587	0.5217	5.0011	0.2750	0.1819	0.0146	0.4569
0.45-E	0.0941	0.1177	0.5027	5.0256	0.0943	0.3643	0.0141	0.4586
0.45-C	0	0.1478	0.5078	5.0110	0	0.4583	0.0142	0.4583

II.1.2 Experimental - Ionic strength $I = 0.78 \text{ mol/kgH}_2\text{O}$

Experimental solutions were prepared from the stock solution (cf. § II.1) using $\text{NaCl}/\text{NaClO}_4$ to maintain a constant ionic strength of $0.78 \text{ mol/kg H}_2\text{O}$ and are displayed in table 2. Samples were prepared by adding in a 10 mL flask or in a 5 mL flask, to a 1 mL or 0.5 mL of the $0.15\text{M UO}_2(\text{NO}_3).6 \text{ H}_2\text{O}$ stock solution, a suitable amount of the solid salts NaCl and NaClO_4 to obtain the desired ionic strength for each series, and 9 mL or 4.5 mL of 0.01 M HClO_4 .

Table 2. Experimental conditions description at $I = 0.78 \text{ mol/kg H}_2\text{O}$

Sample	Mass NaClO_4 (g)	Mass NaCl (g)	Mass UO_2NO_3 (g)	Mass of 0.01M HClO_4 (g)	$[\text{NaClO}_4]$ (mol/kg H_2O)	$[\text{NaCl}]$ (mol/kg H_2O)	$[\text{UO}_2^{2+}]$ (mol/kg H_2O)	Ionic Strength
0.78-A	0.6788	0	0.4733	4.2380	0.7984	0	0.0155	0.7984
0.78-E	0.9040	0.1459	1.0445	8.5270	0.5234	0.2608	0.0169	0.7842
0.78-F	0.5794	0.2634	0.9678	8.6999	0.3321	0.4662	0.0155	0.7983
0.78-B	0.4079	0.0877	0.5173	4.2756	0.4710	0.3131	0.0167	0.7841
0.78-C	0.2289	0.1456	0.5062	4.3343	0.2620	0.5147	0.0162	0.7767
0.78-D	0	0.2188	0.4889	4.4320	0	0.7608	0.0153	0.7608

II.1.3 Experimental - Ionic strength $I = 1.05 \text{ mol/kg H}_2\text{O}$

Samples were prepared by adding in a 10 mL volumetric flask, to a 1 mL of the 0.15M $\text{UO}_2(\text{NO}_3)_6 \cdot \text{H}_2\text{O}$ stock solution (§ II.1), a suitable amount of the solid salts NaCl and NaClO_4 to obtain the desired ionic strength, $I = 1.05 \text{ mol/kg H}_2\text{O}$, for each series, and 9 mL of 0.01 M HClO_4 . In the following table, are displayed the experimental conditions.

Table 3. Experimental conditions description at $I = 1.05 \text{ mol/kg H}_2\text{O}$

Sample	Mass NaClO_4 (g)	Mass NaCl (g)	Mass UO_2NO_3 (g)	Mass of 0.01M HClO_4 (g)	$[\text{NaClO}_4]$ (mol/kg H_2O)	$[\text{NaCl}]$ (mol/kg H_2O)	$[\text{UO}_2^{2+}]$ (mol/kg H_2O)	Ionic Strength
1.05-A	1.8064	0	1.0291	8.2159	1.0828	0	0.0172	1.0828
1.05-D	1.4447	0.1174	1.0421	8.3267	0.8545	0.2144	0.0172	1.0690
1.05-B	1.0856	0.2374	0.9826	8.4483	0.6379	0.4307	0.0161	1.0686
1.05-E	0.7256	0.3518	1.0529	8.5054	0.4207	0.6298	0.0170	1.0505
1.05-F	0.3646	0.4670	1.0285	8.6262	0.2093	0.8277	0.0165	1.0370
1.05-C	0	0.5882	0.9982	8.7279	0	1.0348	0.0159	1.0348

II.1.4 Experimental - Ionic strength $I = 2.48 \text{ mol/kg H}_2\text{O}$

Experimental solutions were prepared from the stock solution (§ II.1) using $\text{NaCl}/\text{NaClO}_4$ to maintain a constant ionic strength of $2.48 \text{ mol/kg H}_2\text{O}$. Samples were prepared as described previously. The experimental conditions are shown in table 4.

Table 4. Experimental conditions description at $I = 2.48 \text{ mol/kg H}_2\text{O}$

Sample	Mass NaClO_4 (g)	Mass NaCl (g)	Mass UO_2NO_3 (g)	Mass of 0.01M HClO_4 (g)	$[\text{NaClO}_4]$ (mol/kg H_2O)	$[\text{NaCl}]$ (mol/kg H_2O)	$[\text{UO}_2^{2+}]$ (mol/kg H_2O)	Ionic Strength
2.48-A	2.2556	0	0.5207	4.501	2.4892	0	0.0161	2.4893
2.48-E	1.9887	0.0876	0.5200	4.515	2.1889	0.2977	0.0160	2.4866
2.48-B	1.8066	0.1454	0.5232	4.504	1.9916	0.4949	0.0161	2.4865
2.48-F	1.6245	2045	0.5209	4.516	1.7871	0.6947	0.0160	2.4818
2.48-C	1.4467	0.2628	0.5213	4.521	1.5900	0.8919	0.0160	2.4819
2.48-G	1.3553	0.2938	0.5213	4.506	1.4939	1.0000	0.0161	2.4940
2.48-H	1.1280	0.3682	0.5188	4.508	1.2434	1.2533	0.0160	2.4967
2.48-D	0.9041	0.4368	0.5220	4.503	0.9970	1.4874	0.0161	2.4844

II.1.5 Experimental - Ionic strength $I = 3.71 \text{ mol/kg H}_2\text{O}$

In table 5 are illustrated the experimental conditions to prepare our solutions from the stock solution (§ II.1).

Table 5. Experimental conditions description at $I = 3.71 \text{ mol/kg H}_2\text{O}$

Sample	Mass NaClO_4 (g)	Mass NaCl (g)	Mass UO_2NO_3 (g)	Mass of 0.01M HClO_4 (g)	$[\text{NaClO}_4]$ (mol/kg H_2O)	$[\text{NaCl}]$ (mol/kg H_2O)	$[\text{UO}_2^{2+}]$ (mol/kg H_2O)	Ionic Strength
3.71-A	5.2154	0	1.0233	6.6268	3.7779	0	0.0207	3.7779
3.71-B	5.0033	0.1198	1.0433	6.7349	3.5646	0.2236	0.0208	3.8282
3.71-C	4.5135	0.2923	1.0446	6.9723	3.1199	0.6239	0.0202	3.7438
3.71-E	4.0604	0.4384	1.0457	7.1128	2.7580	0.9195	0.0199	3.6775
3.71-D	3.6048	0.5838	1.0461	7.2322	2.4131	1.2067	0.0196	3.6198
3.71-F	3.2560	0.7044	1.0523	7.2628	2.1700	1.4496	0.0196	3.6195

II.1.6 Ionic strength $I = 4.98 \text{ mol/kg H}_2\text{O}$

Experimental solutions were prepared from the stock solution (§ II.1) using NaCl/NaClO₄ to maintain a constant ionic strength of 4.98 mol/kg H₂O. Samples were prepared as described previously. The experimental conditions are shown in table 6.

Table 6.: Experimental conditions description at $I = 4.98 \text{ mol/kg H}_2\text{O}$

Sample	Mass NaClO ₄ (g)	Mass NaCl (g)	Mass UO ₂ NO ₃ (g)	Mass of 0.01M HClO ₄ (g)	[NaClO ₄] (mol/kg H ₂ O)	[NaCl] (mol/kg H ₂ O)	[UO ₂ ²⁺] (mol/kg H ₂ O)	Ionic Strength
4.98-A	9.0247	0	1.0471	9.0067	4.9743	0	0.016	4.9743
4.98-G	8.5712	0.1504	1.0532	9.0101	4.7199	0.2557	0.016	4.9756
4.98-B	8.1199	0.2925	1.0447	9.0226	4.4696	0.4972	0.016	4.9668
4.98-H	7.6673	0.4410	1.0469	9.0252	4.2185	0.7492	0.016	4.9677
4.98-I	7.2134	0.5824	1.0495	9.0225	3.9688	0.9895	0.016	4.9582
4.98-C	6.8570	0.7060	1.0457	9.0078	3.7796	1.2016	0.016	4.9813
4.98-J	6.4994	0.8182	1.0593	9.0009	3.5801	1.3917	0.016	4.9718
4.98-K	6.1377	0.9349	1.0510	9.0097	3.3807	1.5901	0.016	4.9708
4.98-L	5.7741	1.0569	1.0457	9.0163	3.1800	1.7974	0.016	4.9774
4.98-D	5.4130	1.1665	1.0437	9.0154	2.9820	1.9843	0.016	4.9664
4.98-M	4.4232	0.0294	0.5210	4.5150	4.8673	0.0999	0.016	4.9671
4.98-N	4.3312	0.0582	0.5223	4.5244	4.7559	0.1973	0.016	4.9532
4.98-O	4.2470	0.0877	0.5222	4.5032	4.6832	0.2986	0.016	4.9818
4.98-P	4.1509	0.1174	0.5175	4.5196	4.5666	0.3988	0.016	4.9654
4.98-Q	4.5112	0	0.5219	4.5133	4.9649	0	0.016	4.9649
4.98-R	4.4389	0.6716	0.5223	4.5252	2.6776	2.2768	0.016	4.9544
4.98-S	2.2579	0.7312	0.5211	4.5016	2.4912	2.2911	0.016	4.9822
4.98-T	2.0751	0.7887	0.5189	4.5069	2.2881	2.6853	0.016	4.9734
4.98-E	1.8028	0.8768	0.5193	4.5071	1.9876	2.9849	0.016	4.9725
4.98-U	1.6247	0.9362	0.5195	4.5222	1.7858	3.1775	0.016	4.9632
4.98-V	1.2647	1.0620	0.5202	4.5030	1.3952	3.6177	0.016	5.0129
4.98-W	0.9925	1.1391	0.5217	4.5007	1.0951	3.8810	0.016	4.9761
4.98-X	0.6312	1.2587	0.5187	4.5336	0.6923	4.2631	0.016	4.9554
4.98-Y	0.4544	1.3146	0.5210	4.5119	0.5003	4.4696	0.016	4.9699
4.98-Z	0.2265	1.3880	0.5189	4.5018	0.2500	4.7306	0.016	4.9806
4.98-F	0	1.4626	0.5212	4.5212	0	4.9676	0.016	4.9676

II.2. Results and Discussion

Selected absorption spectra of U(VI) at a constant ionic strength of 4.98 mol/kg H₂O are plotted in Figure 1 in the wavelength range of 660-330 nm. The spectrum at 0 molal NaCl represents the uranyl ion. With increasing the chloride concentration and maintaining the ionic strength constant, the spectra changed significantly in position and shape. The changes in the spectra appearance were observed for each ionic strength studied. The peak shift was attributed to the formation of chloride complexes. Two different chloride complexes $\text{UO}_2\text{Cl}_n^{2-n}$ with $n = 1, 2$ at $I = 4.98$, were identified up to the experimental chloride concentration of 4.967 molL^{-1} .

Figure 1: Selected UV-Vis absorption spectra of U(VI) at different NaCl/NaClO₄ concentration. $[\text{UO}_2^{2+}] = 0.0161 \text{ m}$, ionic strength = 4.98 mol/kg H₂O.

The UV-Vis absorption spectra of the individual species UO_2^{2+} , UO_2Cl^+ , and UO_2Cl_2 are plotted in Figure 2. The intensities of the spectra are scaled to the same height. The uranyl spectrum was measured directly at 0 molal NaCl and the spectra of UO_2Cl^+ and UO_2Cl_2 were derived from mixed spectra by peak deconvolution.

Figure 2: UV-Vis Absorption spectra of the uranyl ion and the U(VI) chloride species.

To quantify the chloride complexation equilibria, UV-Vis absorption spectra were taken in NaCl/NaClO₄ solutions at constant ionic strengths (0.45, 0.78, 1.05, 2.48, 3.71, and 4.98 mol/kg H₂O). Applying the absorption spectra of the individual species (UO_2^{2+} , $\text{UO}_2\text{Cl}_n^{2-n}$), as given in Figure 2, the mixed spectra were deconvoluted. A typical example is depicted in Figure 3. The spectrum measured at a chloride molality of 1.45 mol/kg H₂O is plotted together with the spectra of the individual components and the residue i.e. the difference between the measured spectrum and the sum of the individual species spectra.

Figure 3: Peak Deconvolution of a mixed spectrum.

In the upper part of Figure 3, the measured spectrum and the spectra of the individual components are plotted. The lower part of Figure 3 shows the difference between the measured spectrum and the summed up spectrum of individual components.

According to the complex formation equilibrium

the thermodynamic formation constants are defined by

$$\beta_0^n = \frac{\gamma_{\text{UO}_2(\text{Cl})_n} m_{\text{UO}_2(\text{Cl})_n}}{\gamma_{\text{UO}_2} \gamma_{\text{Cl}}^n m_{\text{UO}_2} m_{\text{Cl}}^n} = \beta_n \frac{\gamma_{\text{UO}_2(\text{Cl})_n}}{\gamma_{\text{UO}_2} \gamma_{\text{Cl}}^n} \quad (2)$$

where γ_i is the activity coefficient. The mole fraction of the different UO_2^{2+} species and the calculated complex formation constants β_1 and β_2 at each constant ionic strength have been determined.

II.2.1 Ionic strength - 0.45 mol/kg H_2O

Selected Absorption spectra of U(VI) at a constant ionic strength of 0.45 mol/kg H_2O , are plotted in Figure 4, in the wavelength range of 660-330 nm. The spectrum at 0 molal NaCl represents the uranyl ion. With increasing the chloride concentration and maintaining the ionic strength constant, the spectra changed in position and shape.

Figure 4: Selected UV-Vis absorption spectra of U(VI) at different NaCl/NaClO₄ concentration. $[\text{UO}_2^{2+}] = 0.0139\text{m}$, Ionic strength = 0.45 mol/kg H_2O .

The mole fractions of the uranyl ion and the chloride species were deduced from the spectra (Figure 4) by peak deconvolution, and are presented in table 7.

Table 7. Experimentally determined mole fractions χ_i of UO_2^{2+} and UO_2Cl^+ and chloride complex formation constants β_1 at $I = 0.45 \text{ mol/kg H}_2\text{O}$ at 25°C

m_{NaCl} (mol/kg H_2O)	m_{NaClO_4} (mol/kg H_2O)	$m_{\text{U}_{\text{tot}}}$ (mol/kg H_2O)	$\chi_{\text{UO}_2^{2+}}$	$\chi_{\text{UO}_2\text{Cl}^+}$	$\log \beta_1$
0.091	0.365	0.0139	0.960	0.040	-0.338
0.182	0.275	0.0139	0.912	0.088	-0.320
0.364	0.094	0.0139	0.860	0.140	-0.350
0.458	0	0.0139	0.830	0.170	-0.350

Assuming the activity coefficient quotient of Eq. (2) to be constant at given ionic strength, Eq. (2) can be rewritten as

$$\log(m_{\text{UO}_2(\text{Cl})_n}/m_{\text{UO}_2^{2+}}) = \log \beta_n + n \log(m_{\text{Cl}^-}) \quad (3)$$

The ratios of the molalities of the uranyl species are plotted as a function of the chloride molality according to Eq. (3) for the monochloro complex.

In Figure 5, the first complexation constant is plotted as a function of the NaCl molality. A straight line is obtained with the slope of 0.97 ± 0.02 at $I = 0.45 \text{ mol/kg H}_2\text{O}$, which is close to the expected value of 1. These results confirm the postulated complexation equilibrium.

Figure 5: Correlation of the experimentally determined ratio of UO_2Cl^+ with Cl^- molality in the logarithmic scale ($n=1$), at $I = 0.45 \text{ mol/kg H}_2\text{O}$. The solid line is calculated assuming the theoretical slope 1.

II.2.2 Ionic strength - 0.78 mol/kg H₂O

Selected absorption spectra of U(VI) at a constant ionic strength of 0.78 mol/kg H₂O, are presented in Figure 6. With increasing the chloride concentration and maintaining the ionic strength constant, the spectra changed more significantly in position and shape than those observed at I = 0.45 mol/kg H₂O. The formation of the monochloro complex of U(VI) is more notable in this present study. We observed already the growth of the two major peaks indicating the formation of the chloride complex at 456 nm and 471 nm respectively.

Figure 6: Selected UV-Vis absorption spectra of U(VI) at different NaCl/NaClO₄ concentration. [UO₂²⁺] = 0.0155m, Ionic strength = 0.78 mol/kg H₂O.

The mole fractions of the uranyl ion and the chloride species are deduced from the spectra (Figure 6) by peak deconvolution. All results evaluated according to Eq.(2) are summarized in table 8.

Table 8. Experimentally determined mole fractions χ_i of UO_2^{2+} and UO_2Cl^+ and chloride complex formation constants β_1 at $I = 0.78 \text{ mol/kg H}_2\text{O}$ at 25°C .

m_{NaCl} (mol/kg H_2O)	m_{NaClO_4} (mol/kg H_2O)	$m_{\text{U}_{\text{tot}}}$ (mol/kg H_2O)	$\chi_{\text{UO}_2^{2+}}$	$\chi_{\text{UO}_2\text{Cl}^+}$	$\log \beta_1$
0.261	0.523	0.0155	0.915	0.085	-0.448
0.313	0.471	0.0155	0.900	0.100	-0.450
0.466	0.332	0.0155	0.860	0.140	-0.457
0.514	0.262	0.0155	0.840	0.160	-0.432
0.761	0	0.0155	0.790	0.210	-0.457

In Figure 7, according to Eq.(3), the first complexation constant is plotted as a function of the NaCl molality. A straight line is obtained with the slope of 0.99 ± 0.03 at $I = 0.78 \text{ mol/kg H}_2\text{O}$, which is close to the expected value of 1.

Figure 7: Correlation of the experimentally determined ratio of UO_2Cl^+ with Cl^- molality in the logarithmic scale ($n=1$), at $I=0.78 \text{ mol/kg H}_2\text{O}$.

II.2.3 Ionic strength - $1.05 \text{ mol/kg H}_2\text{O}$

Three selected absorption spectra of U(VI) at a constant ionic strength of $1.05 \text{ mol/kg H}_2\text{O}$, are presented in Figure 8. The five maxima observed for the uranyl ion absorption spectrum are situated at 402.6 nm , 413.5 nm , 425.3 nm , 468.4 nm , and 485.6 nm .

Figure 8: Selected UV-Vis absorption spectra of U(VI) at different NaCl/NaClO₄ concentration. [UO₂²⁺] = 0.0172m, Ionic strength = 1.05 mol/kg H₂O

The mole fractions of the uranyl ion and the chloride species are deduced from the spectra (Figure 8) by peak deconvolution. All results evaluated according to Eq.(2) are displayed in table 9.

Table 9. Experimentally determined mole fractions χ_i of UO₂²⁺ and UO₂Cl⁺ chloride complex formation constant β_1 at I = 1.05 mol/kg H₂O at 25 °C.

m_{NaCl} (mol/kg H ₂ O)	m_{NaClO_4} (mol/kg H ₂ O)	$m_{U_{tot}}$ (mol/kg H ₂ O)	$\chi_{UO_2^{2+}}$	$\chi_{UO_2Cl^+}$	$\log \beta_1$
0.214	0.854	0.0172	0.920	0.080	-0.392
0.431	0.638	0.0172	0.860	0.140	-0.422
0.629	0.421	0.0172	0.810	0.190	-0.429
0.827	0.209	0.0172	0.765	0.235	-0.430
1.035	0	0.0172	0.718	0.282	-0.421

In Figure 9, the first complexation constant is plotted as a function of the NaCl molality. A straight line is obtained with the slope of 0.95 ± 0.02 at $I = 1.05 \text{ mol/kg H}_2\text{O}$.

Figure 9: Correlation of the experimentally determined ratio of UO_2Cl^+ with Cl^- molality in the logarithmic scale ($n=1$), at $I=1.05 \text{ mol/kg H}_2\text{O}$

II.2.4 Ionic strength - 2.48 mol/kg H_2O

Selected absorption spectra of U(VI) at a constant ionic strength of 2.48 mol/kg H_2O , are plotted in Figure 10. At the highest NaCl concentration i.e. 1.4874 mol/kg H_2O , the shape of the absorption spectrum indicates already the presence of three species, the uranyl ion, the monochloro complex of U(VI), and the bischloro complex of U(VI). By peak deconvolution, we were able to quantify these three species present in the solution.

The ratios of the molalities of the uranyl species are plotted as a function of the chloride molality according to Eq. (3) for the monochloro complex, and the bischloro complex. In Figure 11, the first and second complexation constants are plotted as a function of the NaCl molality. A straight line is obtained with the slope of 0.98 ± 0.04 , which is close to the expected value of 1, and a slope of 2.19 ± 0.27 , which is close to the expected value of 2.

Figure 11: Correlation of the experimentally determined ratio of UO_2Cl^+ , and UO_2Cl_2 with Cl^- molality in the logarithmic scale ($n=1, 2$ respectively). The solid lines are calculated assuming the theoretical slopes 1 and 2.

II.2.5 Ionic strength - 3.71 mol/kg H_2O

Selected absorption spectra of U(VI) at a constant ionic strength of 3.71 mol/kg H_2O , are plotted in Figure 12 in the NaCl concentration range of 0 to 1.20 m. The spectrum at 0 molal NaCl represents the uranyl ion. As observed previously, the same trend is shown here. The chloride concentration increase changed significantly the absorption spectra in position and shape.

Figure 12: Selected UV-Vis absorption spectra of U(VI) at different NaCl/NaClO₄ concentration. [UO₂²⁺] = 0.020 m, Ionic strength = 3.71 mol/kg H₂O

The mole fractions of the uranyl ion and the chloride species are deduced from the spectra (Figure 12) by peak deconvolution. All results evaluated according to Eq.(2) are summarized in table 11.

Table 11. Experimentally determined mole fractions χ_i of UO₂²⁺, UO₂Cl⁺ and chloride complex formation constants β_1 at I = 3.71 mol/kg H₂O at 25 °C.

m_{NaCl} (mol/kg H ₂ O)	m_{NaClO_4} (mol/kg H ₂ O)	$m_{U_{tot}}$ (mol/kg H ₂ O)	$\chi_{UO_2^{2+}}$	$\chi_{UO_2Cl^+}$	$\log \beta_1$
0.263	3.564	0.0207	0.845	0.154	-0.159
0.624	3.120	0.0202	0.698	0.302	-0.159
0.919	2.758	0.0199	0.605	0.395	-0.149
1.206	2.413	0.0196	0.571	0.428	-0.151

In Figure 13, the first complexation constant is plotted as a function of the NaCl molality. A straight line is obtained with the slope of 1.01 ± 0.01 , which is close to the expected value of 1.

Figure 13: Correlation of the experimentally determined ratio of UO_2Cl^+ with Cl^- molality in the logarithmic scale ($n=1$), at $I=3.71$ mol/kg H_2O .

II.2.6 Ionic strength - 4.98 mol/kg H_2O

The mole fractions of the uranyl ion and the chloride species are deduced from the spectra (Figure 1) by peak deconvolution. All results evaluated according to Eq.(2) are summarized in table 12.

Table 12. Experimentally determined mole fractions χ_i of UO_2^{2+} and UO_2Cl^+ and UO_2Cl_2 chloride complex formation constants β_1 , β_2 at $I = 4.98 \text{ mol/kg H}_2\text{O}$ at 25°C .

m_{NaCl} (mol/kg H_2O)	m_{NaClO_4} (mol/kg H_2O)	m_{Utot} (mol/kg H_2O)	$\chi_{\text{UO}_2^{2+}}$	$\chi_{\text{UO}_2\text{Cl}^+}$	$\chi_{\text{UO}_2\text{Cl}_2}$	$\log \beta_1$	$\log \beta_2$
0.099	4.867	0.0160	0.916	0.084	0	0.039	
0.197	4.756	0.0160	0.845	0.155	0	0.034	
0.255	4.719	0.0161	0.786	0.214	0	0.027	
0.298	4.683	0.0161	0.761	0.239	0	0.036	
0.398	4.566	0.0159	0.730	0.270	0	0.034	
0.497	4.469	0.0162	0.652	0.348	0	0.030	
0.989	3.969	0.0161	0.470	0.502	0.028	0.033	-1.203
1.201	3.779	0.0161	0.420	0.550	0.029	0.037	-1.316
1.391	3.580	0.0163	0.384	0.575	0.041	0.032	-1.255
1.590	3.381	0.0163	0.349	0.592	0.059	0.028	-1.173
1.797	3.180	0.0162	0.321	0.618	0.061	0.030	-1.231
1.984	2.982	0.0161	0.291	0.631	0.078	0.038	-1.170
2.277	2.677	0.0161	0.261	0.648	0.091	0.037	-1.174
2.491	2.491	0.0161	0.245	0.664	0.091	0.037	-1.221
2.685	2.288	0.0161	0.231	0.671	0.098	0.034	-1.231
2.985	1.987	0.0161	0.211	0.685	0.104	0.037	-1.254
3.177	1.786	0.0160	0.201	0.693	0.106	0.035	-1.282
3.881	1.095	0.0161	0.159	0.679	0.161	0.039	-1.173
4.263	0.692	0.0160	0.146	0.679	0.175	0.037	-1.183
4.469	0.500	0.0161	0.140	0.676	0.184	0.033	-1.184
4.730	0.250	0.0161	0.132	0.675	0.193	0.033	-1.189
4.967	0	0.0160	0.125	0.674	0.201	0.035	-1.189

In Figure 14, the first and second complexation constants are plotted as a function of the NaCl molality. A straight line is obtained with the slope of 1.05 ± 0.01 , close to the expected value of 1, and a slope of 2.05 ± 0.06 , close to the expected value of 2.

Figure 14: Correlation of the experimentally determined ratio of UO_2Cl^+ , and UO_2Cl_2 with Cl^- molality in the logarithmic scale ($n=1, 2$ respectively). The solid lines are calculated assuming the theoretical slopes 1 and 2.

II.3 Thermodynamic speciation

In Figure 15, the experimentally determined species distribution are shown at $I = 4.98$ mol/kg H_2O as a function of the NaCl molality. Knowing the uranium total concentration and having determined the U(VI) concentrations by UV-Vis spectroscopy using Beer-Lambert's law, the concentrations of the UO_2Cl^+ and UO_2Cl_2^0 species were deduced from the total uranium concentration and from the uranyl ion concentration, determined previously.

Figure 15: Experimentally determined mole fractions X_i of UO_2^{2+} , UO_2Cl^+ , and UO_2Cl_2 as a function of the NaCl molality at $I = 4.98 \text{ mol/kg H}_2\text{O}$.

II.4 Specific Ion Interaction (SIT) Approach

An intercomparison of the known constants is attempted by introducing ionic strength corrections as demonstrated in the work of Grenthe *et al.* [17]. The SIT is applied to describe the experimentally determined first complexation constant as function of the NaCl molality. According to this approach, a simple relation is deduced for the dependence of an equilibrium constant on ionic strength. The empirical relation applied is originated from the earlier work of Scatchard [18] and later for its broad application refined by Ciavatta [19] and many others [17].

The relation between the thermodynamic constant β_1° at 0 molal ionic strength and the apparent constant β_1 at I_m ionic strength is given by

$$\log_{10} \beta_1 - \Delta z^2 D = \log \beta_1^\circ - \Delta \epsilon I_m \quad (5)$$

where Δz^2 is the difference of the ionic charges, I_m represents the ionic strength in molal scale, ϵ is the ion-ion interaction term for each pair of ions involved in a given system. D is the Debye-Hückel term : $A\sqrt{I_m} / (1+B\bar{a}\sqrt{I_m})$. Since the distance of closest approach ($\bar{a}$) for a given ion-ion interaction is unknown, an empirical value of $B\bar{a} = 1.5$ is suggested by Scatchard [18]. $\Delta\epsilon$ is in fact an empirical parameter for a given multicomponent electrolyte system. The simplicity of Eq.(5) encourages many investigators for its use, rather than by far more sophisticated and complicated approach of Pitzer [20].

The average complexation constants determined from spectroscopic evaluation by peak deconvolution are summarized in table 13.

Table 13. Average complexation constants at different ionic strengths

Ionic strength (mol/kg H ₂ O)	$\log \beta_1$	$\log \beta_2$
I = 0.45	-0.339 ± 0.010	
I = 0.78	-0.449 ± 0.007	
I = 1.05	-0.419 ± 0.012	
I = 2.48	-0.300 ± 0.014	-1.526 ± 0.087
I = 3.71	-0.154 ± 0.005	
I = 4.98	0.034 ± 0.003	-1.214 ± 0.025

In Figure 16, the experimental results according to Eq (5) as well as the literature values [21] are plotted according to this model. The calculated parameters of Eq (5) up to $I_m = 4.98$ at 25 °C are presented in table 14.

Table 14. Calculated parameters for the SIT Model

Δz^2	$\Delta\epsilon$	$\log \beta^0$	Ref.
-4	0.17501	0.20923	this work
-4	0.23408	0.20931	[21]

Figure 16: Calculation of experimental constants according to the SIT formalism.

III. EXPERIMENTS WITH VARIATION OF THE IONIC STRENGTH

III.1. Experimental

The NaCl was purchased from Aldrich Chemicals suprapure (99.99%) and was used without further purification. The source of uranium was UO_2CO_3 , dissolved in 0.1 M HClO_4 . We prepared two sets of experiments, the first one with a total UO_2CO_3 concentration of 0.01 M and the second one of 0.02 M. A 0.1 M HClO_4 stock solution was prepared, which is a sufficient acidic medium to prevent the hydrolysis of uranium. The first stock solution was prepared by dissolving 0.033303 g of $\text{UO}_2(\text{CO}_3)$ in 10.00339 g of 0.1 M HClO_4 . The uranium total molality was 0.0101046 mol/kg H_2O .

For the second stock solution, 0.0352 g of $\text{UO}_2(\text{CO}_3)$ were dissolved in 5.0125 g of 0.1M HClO_4 leading to a uranium total molality of 0.0212778 mol/kg H_2O .

In both experiments, the uranium stock solution previously prepared was filled into a 1 cm UV-Vis cuvette. The NaCl molality in the cuvette, was changed step by step by adding an appropriate amount of NaCl (solid). The composition of the main components was

controlled by weighing the sample cuvette before and after the addition of salt. U(VI) concentration was determined by UV-Vis spectroscopy using Beer-Lambert's law. A stirring bar was introduced into the cuvette in order to facilitate the dissolution of the salt. Each absorption spectrum was taken after 5 mn of stirring. The experimental conditions for the two sets of experiments are described in tables 15 and 16.

Table 15. Experimental conditions description for $[\text{UO}_2\text{CO}_3] = 0.01 \text{ m}$

Sample	Mass before (g)	Mass after (g)	Difference of Mass (g)	Loss of H_2O (g)	Total solution Mass (g)	Total Mass NaCl (g)	$[\text{NaCl}]$ (mol/kg H_2O)
UCI-1	2.2048	3.4266			1.2218	0	0
UCI-2 + magnet 0.0871g	3.42567	3.51377	0.0009	0.00093	1.2209	0.00092	0.01289
UCI-3	3.5130	3.51561	0.0026	0.00077	1.2201	0.00353	0.04951
UCI-4	3.5150	3.51809	0.0031	0.00061	1.2195	0.00662	0.09289
UCI-5	3.51803	3.52293	0.0049	6×10^{-5}	1.2194	0.01152	0.1616
UCI-6	3.52254	3.52593	0.0034	0.00039	1.2190	0.01491	0.2093
UCI-7	3.52585	3.53293	0.0071	8×10^{-5}	1.2190	0.02199	0.3087
UCI-8	3.53269	3.53738	0.0047	0.00024	2.2187	0.02668	0.3746
UCI-9	3.53693	3.54055	0.0036	0.00045	1.2183	0.03030	0.4256
UCI-10	3.54031	3.54650	0.0062	0.00024	1.2180	0.03649	0.5126
UCI-11	3.54599	3.54985	0.0039	0.00051	1.2175	0.04035	0.5671
UCI-12	3.54971	3.55767	0.0080	0.00014	1.2174	0.04831	0.6790
UCI-13	3.55739	3.56283	0.0054	0.00028	1.2171	0.05375	0.7557
UCI-14	3.5625	3.56765	0.0051	0.00033	1.2168	0.05890	0.8283
UCI-15	3.56728	3.57306	0.0058	0.00037	1.2164	0.06468	0.9099
UCI-16	3.57285	3.57827	0.0054	0.00021	1.2162	0.07010	0.9863
UCI-17	3.5779	3.59058	0.0127	0.00037	1.2158	0.08278	1.1650
UCI-18	3.59037	3.59769	0.0073	0.00021	1.2156	0.09010	1.2683

Table 16. Description of the experimental conditions for $[\text{UO}_2\text{CO}_3] = 0.02 \text{ m}$

Sample	Mass before (g)	Mass after (g)	Difference of Mass (g)	Loss of H_2O (g)	Total solution Mass (g)	Total Mass NaCl (g)	$[\text{NaCl}]$ (mol/kg H_2O)
UCI-21	2.2950	3.5143			1.2193	0	0
UCI-22	3.51425	3.52466	0.0104	5×10^{-5}	1.21925	0.00592	0.0831
UCI-23	3.52067	3.53156	0.0109	0.00399	1.21526	0.01681	0.2367
UCI-24	3.53086	3.53773	0.0069	0.0007	1.21456	0.02368	0.3336
UCI-25	3.53722	3.54983	0.0126	0.00051	1.21405	0.03629	0.5115
UCI-26	3.54967	3.55322	0.0036	0.00016	1.21389	0.03984	0.5616
UCI-27	3.55298	3.55996	0.0070	0.00024	1.21365	0.04682	0.6601
UCI-28	3.55961	3.56886	0.0092	0.00035	1.21330	0.05607	0.7908
UCI-29	3.56845	3.57654	0.0081	0.00041	1.21289	0.06416	0.9052
UCI-30	3.57621	3.59076	0.0145	0.00033	1.21256	0.07871	1.1108
UCI-31	3.58982	3.60214	0.0123	0.00094	1.21162	0.09103	1.2856
UCI-32	3.60181	3.61248	0.0107	0.00033	1.21129	0.1017	1.4367
UCI-33	3.61210	3.62054	0.0084	0.00038	1.21091	0.11014	1.5564
UCI-34	3.61962	3.63267	0.0131	0.00092	1.20999	0.12319	1.7421
UCI-35	3.63222	3.64839	0.0162	0.00045	1.20954	0.13936	1.9715
UCI-36	3.64794	3.66070	0.0128	0.00045	1.20909	0.15212	2.1529
UCI-37	3.66043	3.67236	0.0119	0.00027	1.20882	0.16405	2.3222
UCI-38	3.67167	3.68774	0.0161	0.00069	1.20813	0.18012	2.5512
UCI-39	3.68739	3.71390	0.0265	0.00035	1.20778	0.20663	2.9275

III.2. Results and discussion for $[\text{UO}_2\text{CO}_3] = 0.01 \text{ m}$

To quantify the chloride complexation equilibria, UV-Vis absorption spectra were taken in NaCl solution. Applying the absorption spectra of the individual species (UO_2^{2+} , $\text{UO}_2\text{Cl}_n^{2-n}$, $n = 1, 2$), as given in Figure 2, the mixed spectra were deconvoluted (Figure 17). The spectrum measured at a chloride molality of 0.512 mol/kg H_2O is plotted together with (1) the spectra of the individual components, (2) the residue i.e. the difference between the measured spectrum and the sum of the individual species spectra, and (3) the fitting curve corresponding to the sum of the individual species spectra. Between 330 nm and 400 nm, the fitting curve could not describe the UV-Vis measured spectrum properly. We assumed that the formation of colloids particles within the solution was responsible of the shift of the absorption spectrum. All the spectra were fitted from 400 nm to 600 nm, assuming that before 400 nm, the error in the fitting stayed negligible. The fit of the spectra was good and low residues were produced (Figure 17).

Figure 17: Peak Deconvolution of a mixed spectrum, $[U(VI)] = 0.0101m$, $[NaCl] = 0.512 m$.

According to the complex formation equilibrium

the complex formation constants β_1 and β_2 are calculated at each given NaCl molality by

$$\beta_n = \frac{\chi_{UO_2Cl_n^{2-n}}}{\chi_{UO_2^{2+}} * m_{Cl^-}^n} \quad (6)$$

where χ_i is the mole fraction of the uranium species and m_{Cl} is the molality of Cl^- . The results are summarized in table 17.

Table 17. Experimentally determined mole fractions χ_i of UO_2^{2+} and UO_2Cl^+ and the chloride complex formation constant β_1 in NaCl solution at 25 °C.

m_{NaCl} (mol/kg H_2O)	m_{Utot} (mol/kg H_2O)	$\chi_{\text{UO}_2^{2+}}$	$\chi_{\text{UO}_2\text{Cl}^+}$	$\log \beta_1$
0.308	0.0101	0.917	0.083	-0.534
0.374	0.0101	0.906	0.094	-0.558
0.425	0.0101	0.884	0.116	-0.511
0.512	0.0101	0.867	0.133	-0.525
0.567	0.0101	0.862	0.138	-0.548
0.679	0.0101	0.840	0.160	-0.551
0.755	0.0101	0.829	0.171	-0.563
0.828	0.0101	0.815	0.189	-0.563
0.910	0.0101	0.801	0.199	-0.563
0.986	0.0101	0.779	0.221	-0.541
1.165	0.0101	0.719	0.281	-0.474
1.268	0.0101	0.697	0.303	-0.465

In Figure 18, the chloride complex formation constants are plotted as a function of the NaCl molality. If we compare the value of the first complexation constant obtained at $I = 1.05 \text{ mol/kgH}_2\text{O}$, $\log \beta_1 = -0.430$ and the value obtained here, $\log \beta_1 = -0.474$ for $m_{\text{NaCl}} = 1.165 \text{ mol/kg H}_2\text{O}$, the overall uncertainty of the complex formation constant is estimated to be ± 0.1 logarithmic unit.

Figure 18: The first complexation constant of U(VI) as function of the NaCl molality.

$[\text{UO}_2^{2+}] = 0.0101\text{m}$ in 0.1M HClO_4 .

III.3. Results and discussion for $[\text{UO}_2\text{CO}_3] = 0.02\text{ m}$

The spectrum measured at a chloride molality of $2.15\text{ mol/kg H}_2\text{O}$ is plotted together with the spectra of the individual components (Figure 19). Between 330 nm and 410 nm , the UV-Vis absorption spectrum could not be fitted properly. As indicated by the shape of the residue, the most plausible reason could be the presence of a carbonato-chloro complex of U(VI). This specie would be responsible of the difficulty encountered to fit the absorption spectra at the low wavelengths ($300 - 410\text{ nm}$). Therefore, all the spectra were fitted from 410 nm to 600 nm .

Figure 19: Peak Deconvolution of a mixed spectrum, [U(VI)] = 0.0211 m, [NaCl] = 2.1531 m.

According to the complex formation equilibrium

the complex formation constants β_1 and β_2 are calculated at each given NaCl molality by

$$\beta_n = \frac{\chi_{\text{UO}_2\text{Cl}_n^{2-n}}}{\chi_{\text{UO}_2^{2+}} * m_{\text{Cl}^-}^n} \quad (6)$$

where χ_i is the mole fraction of the Uranium species and m_{Cl^-} is the molality of Cl^- . The results are summarized in table 18.

Table 18. Experimentally determined mole fractions χ_i of UO_2^{2+} and UO_2Cl^+ and UO_2Cl_2 chloride complex formation constants β_1 , β_2 in NaCl solutions at 25 °C.

m_{NaCl} (mol/kg H_2O)	$m_{\text{U}_{\text{tot}}}$ (mol/kg H_2O)	$\chi_{\text{UO}_2^{2+}}$	$\chi_{\text{UO}_2\text{Cl}^+}$	$\chi_{\text{UO}_2\text{Cl}_2}$	$\log \beta_1$	$\log \beta_2$
0.083	0.021	0.960	0.040	0	-0.298	
0.236	0.021	0.937	0.063	0	-0.545	
0.333	0.021	0.906	0.094	0	-0.509	
0.511	0.021	0.846	0.154	0	-0.450	
0.561	0.021	0.836	0.164		-0.457	
0.660	0.021	0.826	0.174		-0.496	
0.791	0.021	0.806	0.194		-0.516	
1.110	0.021	0.706	0.294		-0.426	
1.285	0.021	0.691	0.309		-0.458	
1.436	0.021	0.655	0.345		-0.437	
1.556	0.021	0.625	0.374		-0.415	
1.742	0.021	0.615	0.368	0.016	-0.464	-2.054
1.971	0.021	0.595	0.383	0.021	-0.485	-2.035
2.153	0.021	0.555	0.408	0.036	-0.466	-1.849
2.322	0.021	0.495	0.446	0.058	-0.411	-1.665
2.551	0.021	0.475	0.461	0.063	-0.420	-1.692
2.927	0.021	0.446	0.488	0.066	-0.427	-1.762

In Figure 20, the chloride complex formation constants are plotted as a function of the NaCl molality. For comparison, we found $\log \beta_1 = -0.419$ at constant ionic strength of 1.05 mol/kg H_2O . In this particular set of experiments we found $\log \beta_1 = 0.459$ which is in the overall uncertainty of the first complex formation constant, estimated to be ± 0.1 logarithmic unit.

For the second complexation constant, the only possible comparison was for $m_{\text{NaCl}} = 2.48$ mol/kg H_2O , where we found $\log \beta_2 = -1.683$ in this experiment, and $\log \beta_2 = -1.526$ at constant ionic strength 2.48 mol/kg H_2O . The overall uncertainty of the second complex formation constant was estimated to be ± 0.15 logarithmic unit.

Figure 20: The first and second complexation constants of U(VI) as function of the NaCl molality.

$[\text{UO}_2^{2+}] = 0.0211 \text{ m}$ in 0.1 M HClO_4 .

IV. CONCLUSION

The dioxouranium (VI) chloride complexes are very weak. This accounts for a large part of the scattering of the experimental data summarized in Figure 21. A lot of literature data for the chloride complexation of U(VI) have been determined by indirect methods such as distribution between two phases or electromotive force at different ionic strengths [21].

Figure 21: Comparison of $\log \beta_1$ with literature data [21] for U(VI) chloride complex at various ionic strengths.

At $I = 2.48 \text{ mol/kg H}_2\text{O}$, our value $\log \beta_1 = -0.300 \pm 0.014$ is about 0.24 logarithmic unit lower than the literature data [15]. Otherwise, in the ionic strength range 0.45 to 1 mol/kg H_2O , our data were 0.1 logarithmic unit lower than the general trend of those literature data [21]. The deviation can only partly be attributed to the effect of different ionic media. In general, the complex formation constants determined by spectroscopic methods are much smaller than those derived from other methods such as solvent extraction. The latter methods account for an overall effect which considers in addition to the ("inner sphere") chloride complexation, the formation of outer sphere complexes or so-called solvent-separated ion pairs [22].

Figure 22: Comparison of $\log \beta_2$ with literature data [21] for U(VI) bischloro complex at various ionic strengths.

In Figure 22, we compared the literature data [21] with our $\log \beta_2$ values. The literature data for the formation of the bischloro complex of U(VI), $\log \beta_2$, are in general 0.5 logarithmic unit higher than our result. This difference is attributed to a different ionic medium applied.

As we have seen, the understanding of actinide solution chemistry in brines is essential for modeling requiring accurate knowledge of the interaction between UO_2^{2+} and chloride ions. The estimate of the concentration of ligands in the WIPP brine is displayed in table 19.

Table 19. Estimate of the concentration of the ligands in WIPP Brine

Ligand	Concentration
Chloride	5.0 - 6.0 M
Sulfate	0.04 - 0.3 M
Carbonate	1 M
Acetate	7 mM
Citrate	100 μ M
EDTA	1 μ M
α -Hydroxyisobutyrate	400 nM
Lactate	200 μ M
Oxalate	9 mM
Oxine	100 μ M
1, 10 Phenanthroline	400 nM
TTA	20 μ M

For the concentration expected in natural systems, such as the WIPP, where the concentration of chloride ions is expected to be between 5.0 M and 6.0 M, the monochloro complex of U(VI) is important, as well as the bischloro complex of U(VI). Extrapolation methods such as the SIT approach [17] is working in this present situation, until 3 m chloride concentration. The further possibility seems to be extrapolation by Pitzer approach [20].

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