Electronic Supporting Information (ESI)

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S1 Figures

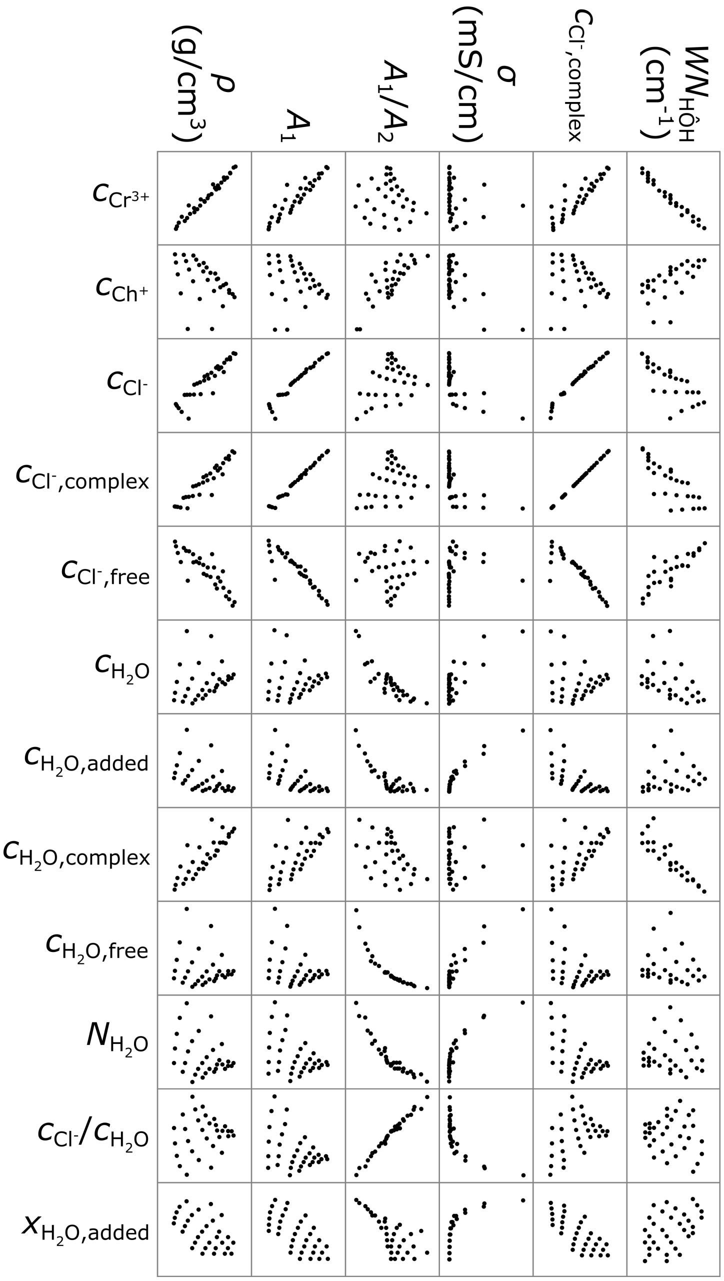


Figure S1: Illustration of the correlations between all values of interest. The corresponding Pearson's r-values are presented in table S2. However, it should be considered that the Pearson's correlation value will only indicate linear trends, non-linear (e.g. quadratic) correlations will not necessarily give high r-values. All concentrations are in mol/L.

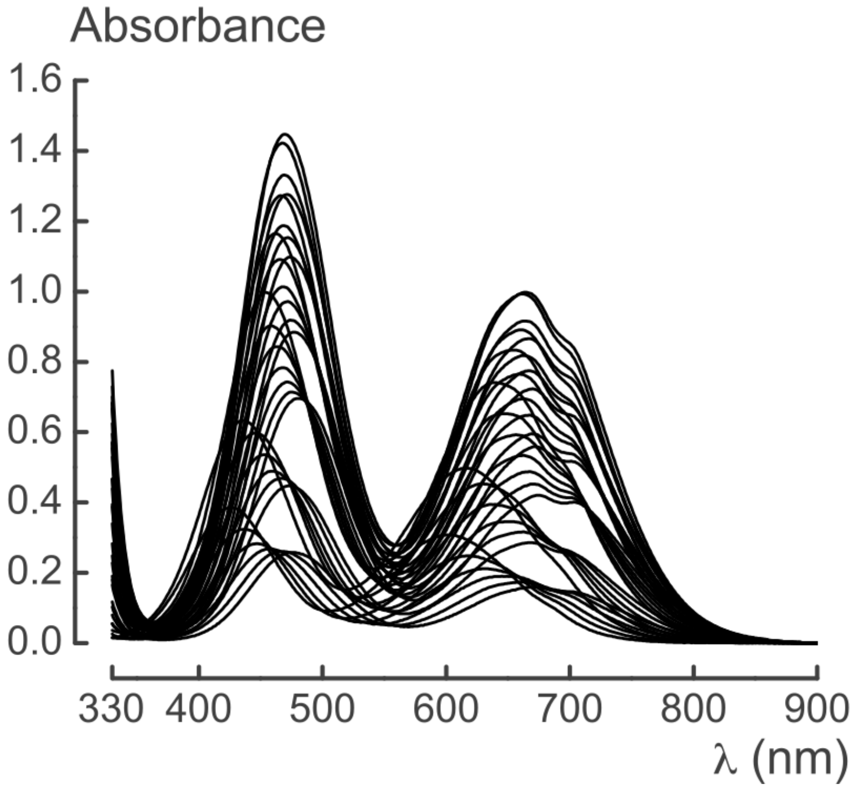
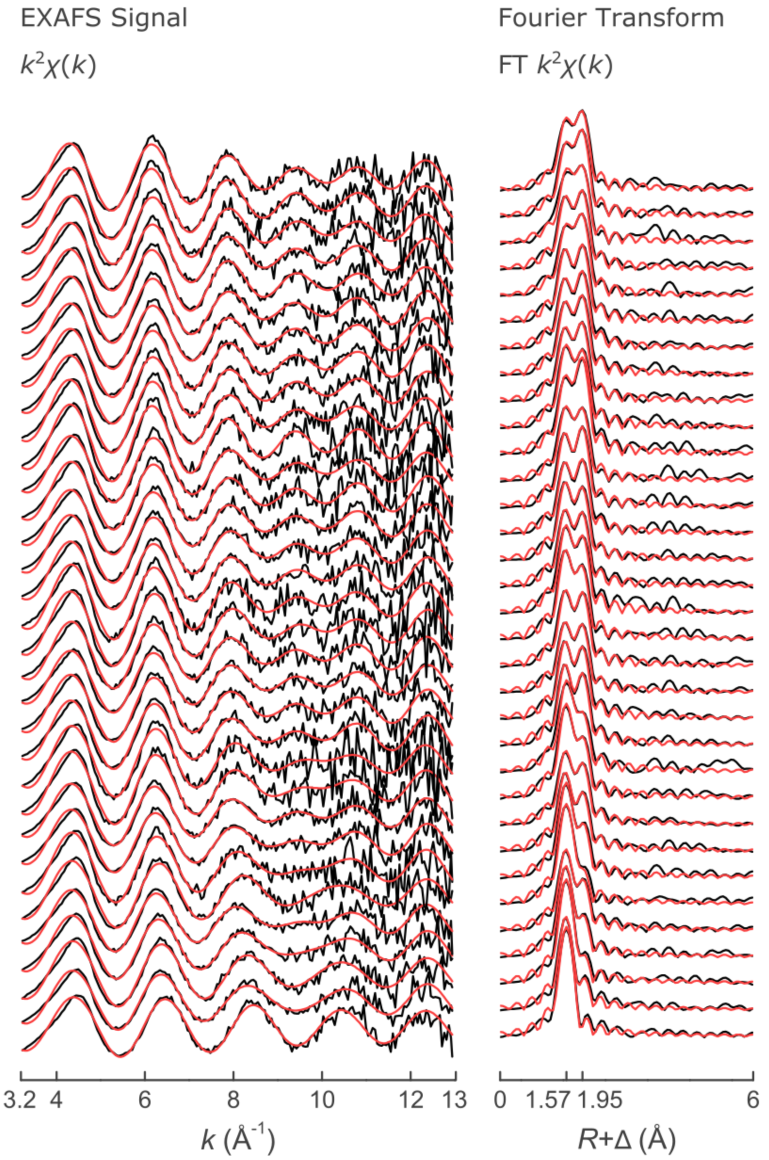


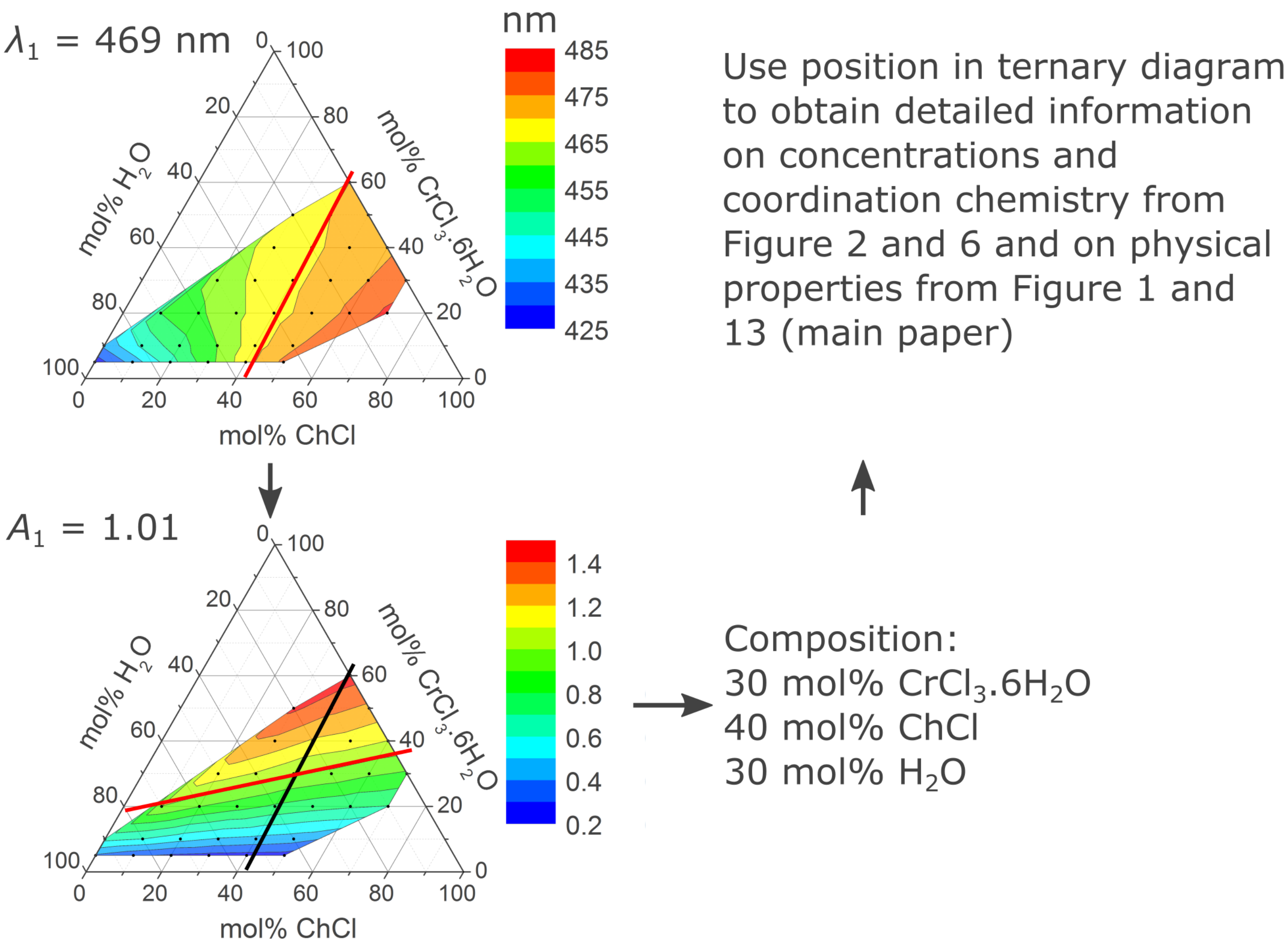
Figure S2: Overview of the UV/Vis spectra of 33 different DES-water compositions. Each spectrum is the average of the measurement of at least 3 DES-water mixtures with the same composition to ensure reproducibility.



Composition (mol%)			Fitted N		Expected N*	
ChCl	$CrCl_3 \cdot 6H_2O$	H_2O	N_O	N_{Cl^-}	N_O	N_{Cl^-}
70	30	0	2.97	3.03	2.75	3.25
70	20	10	2.87	3.13	2.61	3.39
60	40	0	3.04	2.96	2.94	3.06
60	30	10	3.02	2.98	2.89	3.11
60	20	20	2.90	3.10	2.84	3.16
50	50	0	3.05	2.95	3.03	2.97
50	40	10	2.99	3.01	3.03	2.97
50	30	20	3.01	2.99	3.03	2.97
50	**20**	**30**	**3.03**	**2.97**	**3.03**	**2.97**
50	10	40	3.22	2.78	2.94	3.06
50	5	45	2.80	3.20	2.84	3.16
40	60	0	3.16	2.84	3.13	2.87
40	50	10	3.03	2.97	3.13	2.87
40	40	20	3.09	2.91	3.17	2.83
40	30	30	3.24	2.76	3.17	2.83
40	20	40	3.19	2.81	3.22	2.78
40	10	50	3.32	2.68	3.22	2.78
40	5	55	3.41	2.59	3.22	2.78
30	50	20	3.19	2.81	3.22	2.78
30	40	30	3.19	2.81	3.27	2.73
30	30	40	3.26	2.74	3.31	2.69
30	20	50	3.34	2.66	3.41	2.59
30	10	60	3.73	2.27	3.60	2.40
30	5	65	3.75	2.25	3.69	2.31
20	30	50	3.42	2.58	3.50	2.50
20	20	60	3.60	2.40	3.64	2.36
20	10	70	3.94	2.06	3.92	2.08
20	5	75	4.38	1.62	4.16	1.84
10	20	70	3.82	2.18	3.83	2.17
10	10	80	4.21	1.79	4.25	1.75
10	5	85	4.67	1.33	4.68	1.32
0	10	90	4.61	1.39	4.72	1.28
0	5	95	5.33	0.67	5.15	0.85

*Coordination number expected from UV/Vis spectroscopy (vide supra)

Figure S3: All samples studied by UV/Vis were also analyzed by the use of X-ray absorption spectroscopy. The fitted coordination numbers correspond well with the average number of oxygens and chlorides in the first coordination sphere of the complexes, calculated based on the UV/Vis spectroscopy results. Both the experimental (black) and fitted curves (red) are shown. Inherently to the EXAFS equation, the amplitude reduction factor S_0^2 and the coordination numbers are 100% correlated. To solve this problem, the total coordination number of each complex was fixed to 6. Hence, one shell can be optimized as x, while the other is fixed to $6 - x$. However, there still exists a strong correlation between the Debye-Waller factors and these relative coordination numbers. Hence, the values indicated in bold were used as the reference EXAFS and Fourier transform (FT) spectra for the calculation of the Debye-Waller factors, while fixing the coordination numbers to those obtained by UV/Vis spectroscopy. The obtained Debye-Waller factors were then used for all other fitting procedures. The output parameters of all fits can be found in table S1.



Use position in ternary diagram to obtain detailed information on concentrations and coordination chemistry from Figure 2 and 6 and on physical properties from Figure 1 and 13 (main paper)

Composition:
30 mol% $CrCl_3.6H_2O$
40 mol% ChCl
30 mol% H_2O

Figure S4: Illustration on how to use the wavelength and absorbance value of the first absorption band of an unknown DES-water mixture to determine the composition and eventually obtain a lot of information on the concentrations and properties of the liquid. In this example, the unknown sample has a λ_1-value of 469 nm. This value can be used to draw a line in the ternary diagram (red line). Next, in the second ternary diagram, the absorbance value of 1.01 can be used to draw another line which is intersecting with the previous one. In this way, the intersection can be used to determine the composition of the DES-water mixture, which is in this case: $30\,CrCl_3 \cdot 6\,H_2O/40\,ChCl/30\,H_2O$. This composition can then be used to obtain a large range of concentrations, information on the coordination chemistry, and physical properties from the other ternary diagrams in the main paper.

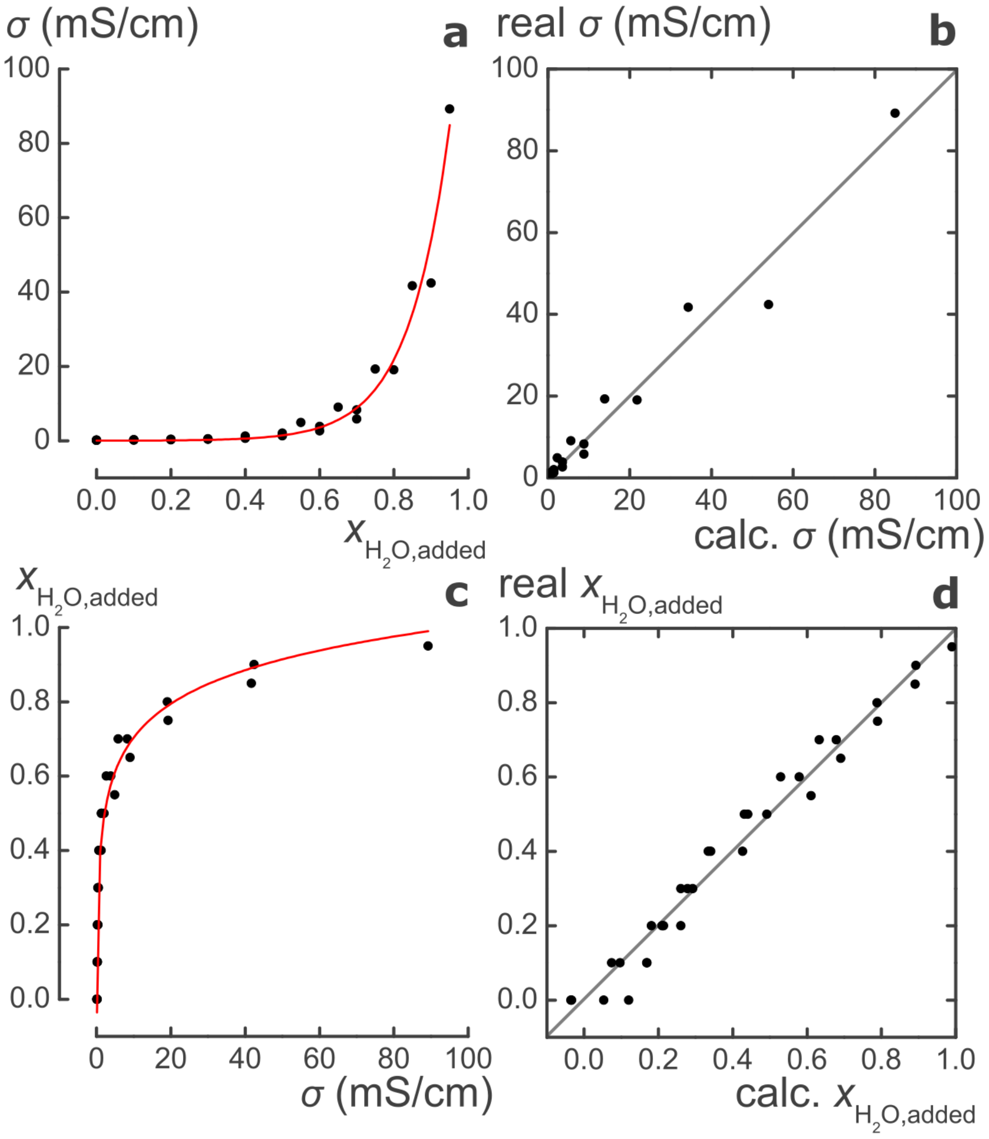


Figure S5: In this figure, the link between the conductivity and the mole fraction of water which was added to the DES-water mixture is studied. (a) shows the conductivity as a function of this mole fraction, which fit has an adjusted R^2 value of 0.97276. The calculated results from eq. 9 are compared with the real conductivities in (b). In (c), the parameters of (a) are interchanged which fit results in an adjusted R^2 value of 0.96977. The accuracy of the corresponding calculations (eq. 10) is illustrated in (d).

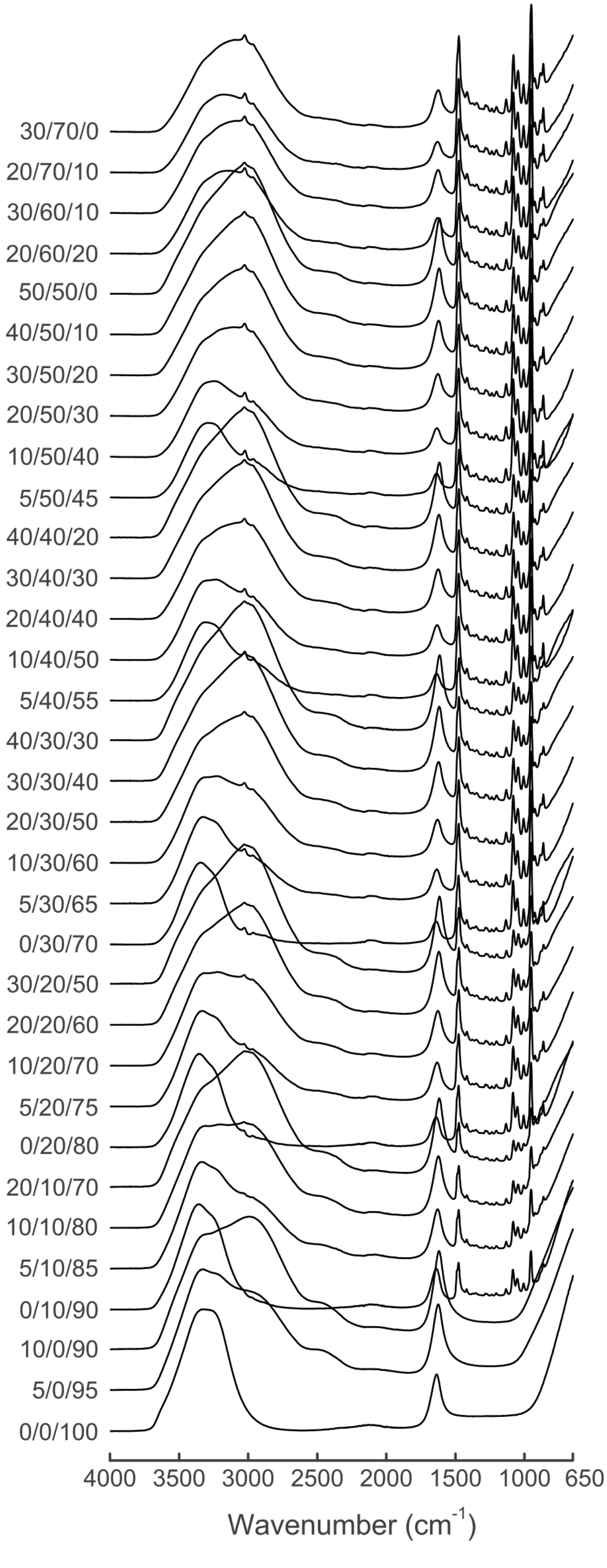


Figure S6: Overview of the attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra for 33 different compositions. Each spectrum is an average of 4 measurements performed on 2 different samples with the same composition. The labels represent the mole percentages of the different components according to: $x\mathrm{CrCl_3 \cdot 6\,H_2O}/y\mathrm{ChCl}/z\mathrm{H_2O}$.

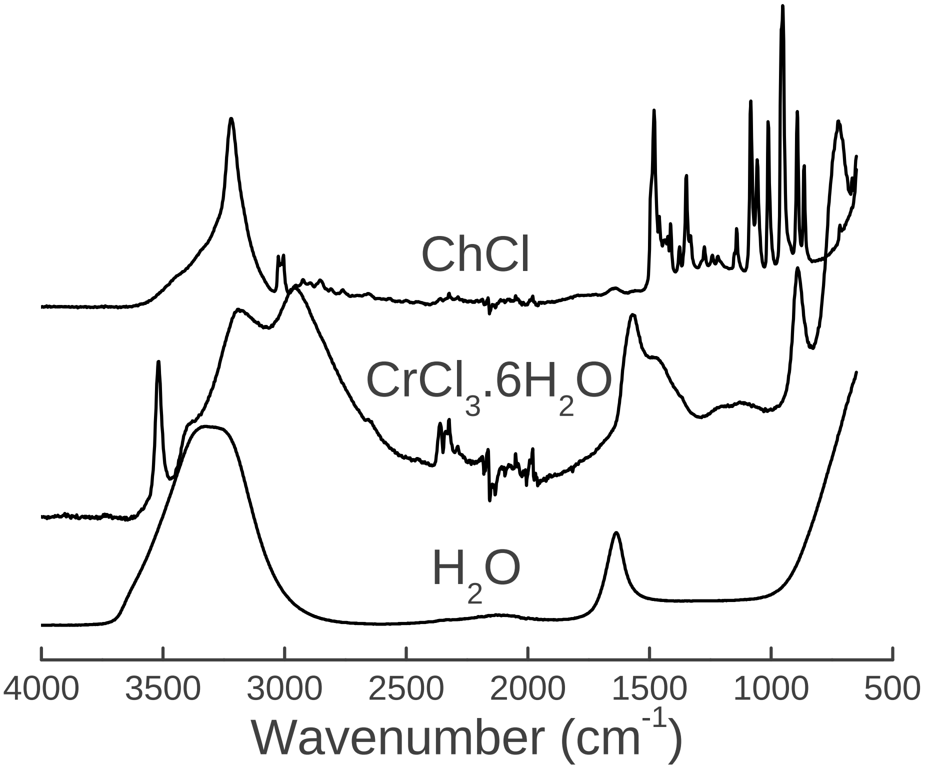


Figure S7: ATR-FTIR spectra of solid choline chloride, solid $CrCl_3 \cdot 6\,H_2O$, and water.

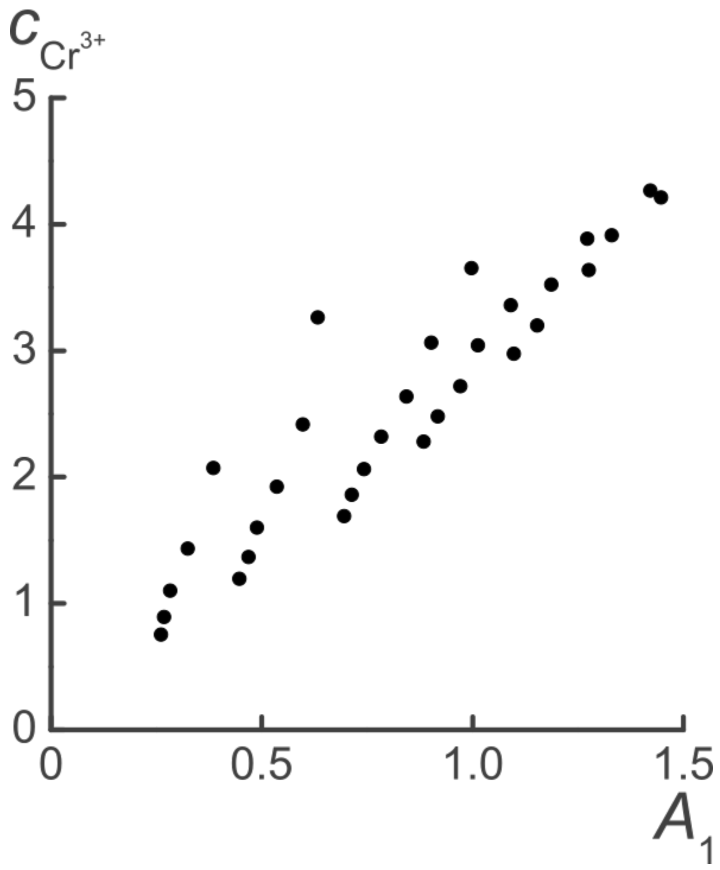
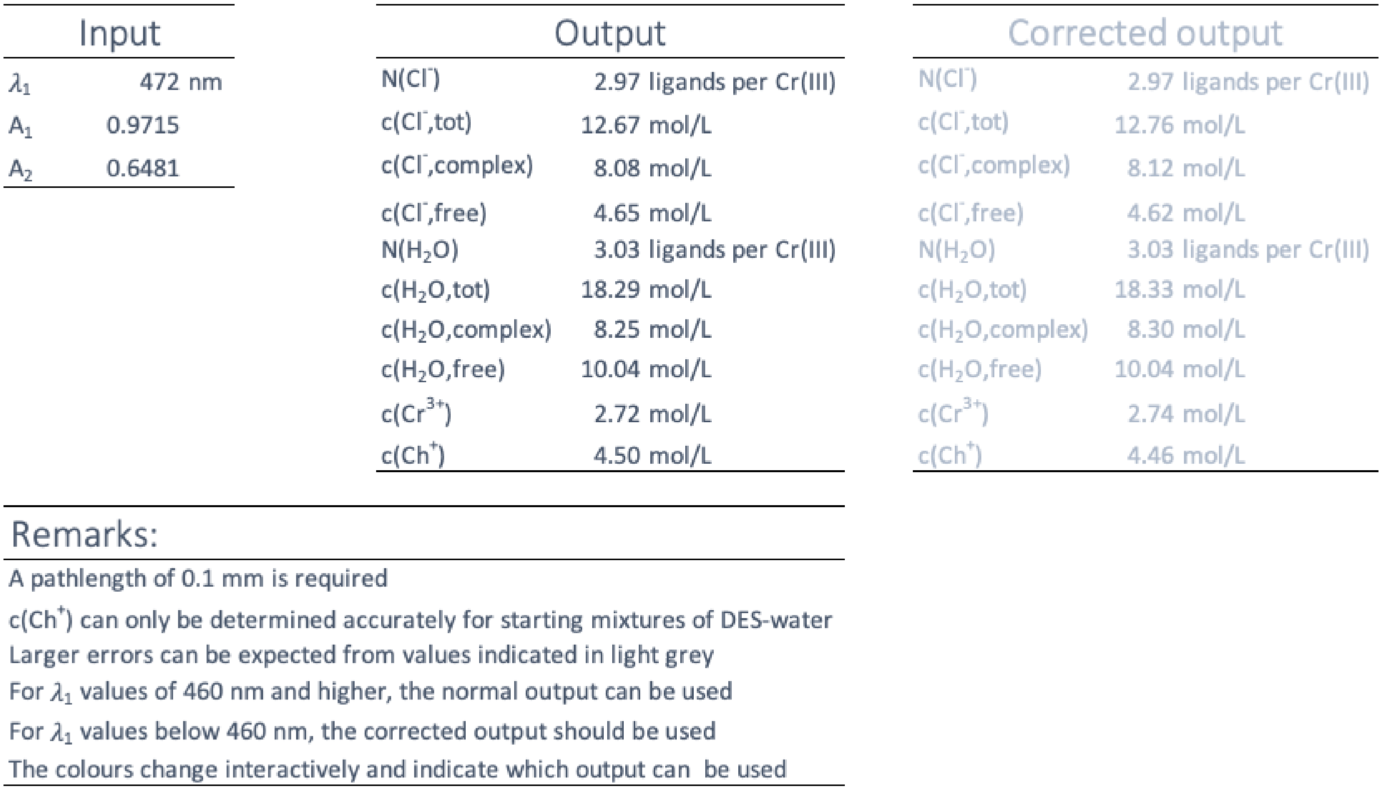


Figure S8: Illustration of the fact that the absorbance is not only influenced by the concentration of chromium(III), but also by its coordination chemistry. This results in the relatively low Pearson's r value of 0.931.



Input	
λ_1	472 nm
A_1	0.9715
A_2	0.6481

Output	
N(Cl^-)	2.97 ligands per Cr(III)
c(Cl^-,tot)	12.67 mol/L
c(Cl^-,complex)	8.08 mol/L
c(Cl^-,free)	4.65 mol/L
N(H_2O)	3.03 ligands per Cr(III)
c(H_2O,tot)	18.29 mol/L
c(H_2O,complex)	8.25 mol/L
c(H_2O,free)	10.04 mol/L
c(Cr^{3+})	2.72 mol/L
c(Ch^+)	4.50 mol/L

Corrected output	
N(Cl^-)	2.97 ligands per Cr(III)
c(Cl^-,tot)	12.76 mol/L
c(Cl^-,complex)	8.12 mol/L
c(Cl^-,free)	4.62 mol/L
N(H_2O)	3.03 ligands per Cr(III)
c(H_2O,tot)	18.33 mol/L
c(H_2O,complex)	8.30 mol/L
c(H_2O,free)	10.04 mol/L
c(Cr^{3+})	2.74 mol/L
c(Ch^+)	4.46 mol/L

Remarks:

A pathlength of 0.1 mm is required

c(Ch^+) can only be determined accurately for starting mixtures of DES-water

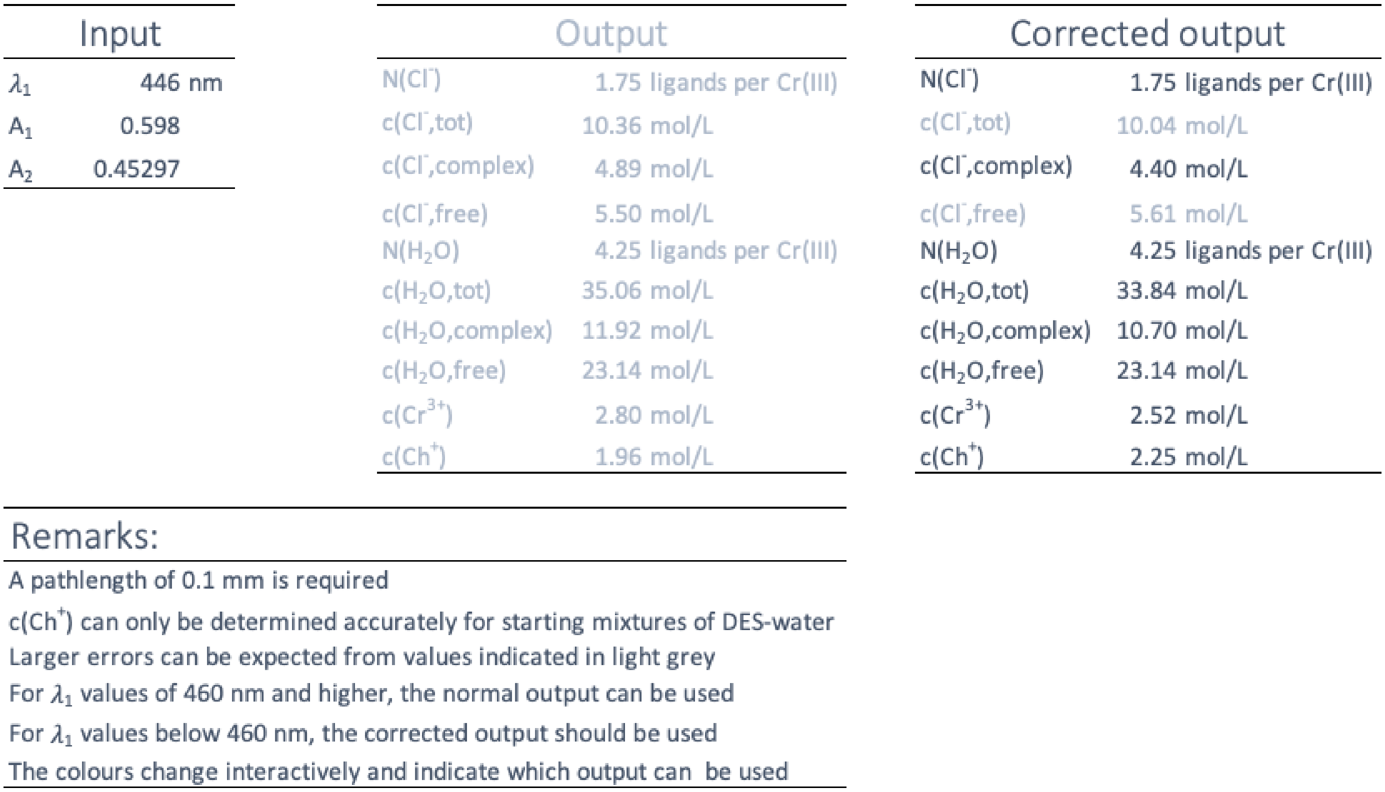
Larger errors can be expected from values indicated in light grey

For λ_1 values of 460 nm and higher, the normal output can be used

For λ_1 values below 460 nm, the corrected output should be used

The colours change interactively and indicate which output can be used

Figure S9: Screenshot of the tool discussed in the main paper. As an example, the λ_1, A_1, and A_2 values of a sample inside the boundary conditions is used. In this case, the regular output should be used. Therefore the corrected output is presented in light gray.



Input	
λ_1	446 nm
A_1	0.598
A_2	0.45297

Output	
$N(Cl^-)$	1.75 ligands per Cr(III)
$c(Cl^-,tot)$	10.36 mol/L
$c(Cl^-,complex)$	4.89 mol/L
$c(Cl^-,free)$	5.50 mol/L
$N(H_2O)$	4.25 ligands per Cr(III)
$c(H_2O,tot)$	35.06 mol/L
$c(H_2O,complex)$	11.92 mol/L
$c(H_2O,free)$	23.14 mol/L
$c(Cr^{3+})$	2.80 mol/L
$c(Ch^+)$	1.96 mol/L

Corrected output	
$N(Cl^-)$	1.75 ligands per Cr(III)
$c(Cl^-,tot)$	10.04 mol/L
$c(Cl^-,complex)$	4.40 mol/L
$c(Cl^-,free)$	5.61 mol/L
$N(H_2O)$	4.25 ligands per Cr(III)
$c(H_2O,tot)$	33.84 mol/L
$c(H_2O,complex)$	10.70 mol/L
$c(H_2O,free)$	23.14 mol/L
$c(Cr^{3+})$	2.52 mol/L
$c(Ch^+)$	2.25 mol/L

Remarks:

A pathlength of 0.1 mm is required

$c(Ch^+)$ can only be determined accurately for starting mixtures of DES-water

Larger errors can be expected from values indicated in light grey

For λ_1 values of 460 nm and higher, the normal output can be used

For λ_1 values below 460 nm, the corrected output should be used

The colours change interactively and indicate which output can be used

Figure S10: Screenshot of the tool discussed in the main paper. As an example, the λ_1, A_1, and A_2 values of a sample outside the boundary conditions is used. In this case, the corrected output should be used. Therefore the regular output is presented in light gray.

S2 Tables

Table S1: Detailed fitting results of the EXAFS experiment shown in fig. S3. The error values are shown in grey, underlined values were fixed during the optimisation, and the EXAFS experiment indicated in bold was used as a reference to calculate the Debye-Waller factors for the other fitting procedures. Table continues on next page.

mol% ChCl	mol% $CrCl_3 \cdot 6\,H_2O$	mol% H_2O	S_0^2	N_O	N_{Cl^-}	R_O (Å)	R_{Cl^-} (Å)	σ_O^2 (Å^2)	$\sigma_{Cl^-}^2$ (Å^2)	E_0 (eV)	F (%)
0	5	95	0.52	5.33	0.67	1.964	2.232	0.0012	0.0027	0.49	30.82
			0.08	0.79		0.003	0.013			0.70	
0	10	90	0.52	4.61	1.39	1.970	2.270	0.0012	0.0027	0.92	33.82
			0.04	0.34		0.003	0.006			0.63	
10	5	85	0.57	4.67	1.33	1.971	2.257	0.0012	0.0027	0.73	32.91
			0.04	0.35		0.003	0.007			0.65	
10	10	80	0.55	4.21	1.79	1.977	2.275	0.0012	0.0027	1.17	34.58
			0.03	0.26		0.003	0.005			0.62	
10	20	70	0.53	3.82	2.18	1.986	2.288	0.0012	0.0027	1.72	35.91
			0.02	0.22		0.004	0.004			0.62	
20	5	75	0.58	4.38	1.62	1.977	2.262	0.0012	0.0027	0.41	37.82
			0.04	0.32		0.004	0.006			0.74	
20	10	70	0.60	3.94	2.06	1.986	2.287	0.0012	0.0027	2.20	44.83
			0.04	0.30		0.005	0.006			0.81	
20	20	60	0.54	3.60	2.40	1.982	2.288	0.0012	0.0027	1.24	34.42
			0.02	0.19		0.003	0.004			0.59	
20	30	50	0.53	3.42	2.58	1.990	2.293	0.0012	0.0027	1.79	32.96
			0.02	0.17		0.004	0.003			0.56	
30	5	65	0.63	3.75	2.25	1.991	2.288	0.0012	0.0027	1.77	41.81
			0.03	0.26		0.004	0.005			0.75	
30	10	60	0.60	3.73	2.27	1.996	2.290	0.0012	0.0027	2.64	56.92
			0.05	0.39		0.007	0.008			1.14	
30	20	50	0.59	3.34	2.66	1.984	2.291	0.0012	0.0027	1.25	34.81
			0.02	0.18		0.004	0.004			0.60	
30	30	40	0.58	3.26	2.74	1.986	2.292	0.0012	0.0027	1.24	35.83
			0.02	0.18		0.004	0.004			0.62	
30	40	30	0.53	3.19	2.81	1.989	2.292	0.0012	0.0027	1.34	31.16
			0.02	0.16		0.004	0.003			0.54	
30	50	20	0.57	3.19	2.81	1.993	2.298	0.0012	0.0027	2.46	41.19
			0.02	0.22		0.005	0.004			0.73	

mol% ChCl	mol% $CrCl_3 \cdot 6\,H_2O$	mol% H_2O	S_0^2	N_O	N_{Cl^-}	R_O (Å)	R_{Cl^-} (Å)	σ_O^2 (Å^2)	$\sigma_{Cl^-}^2$ (Å^2)	E_0 (eV)	F (%)
40	5	55	0.64	3.41	2.59	1.987	2.285	0.0012	0.0027	0.77	39.85
			0.03	0.21		0.005	0.004			0.73	
40	10	50	0.64	3.32	2.68	1.995	2.296	0.0012	0.0027	2.40	50.87
			0.04	0.29		0.006	0.006			0.96	
40	20	40	0.58	3.19	2.81	1.990	2.292	0.0012	0.0027	1.40	32.82
			0.02	0.16		0.004	0.003			0.57	
40	30	30	0.59	3.24	2.76	1.990	2.293	0.0012	0.0027	1.14	35.05
			0.02	0.18		0.004	0.004			0.61	
40	40	20	0.55	3.09	2.91	1.989	2.295	0.0012	0.0027	1.48	35.05
			0.02	0.17		0.004	0.003			0.61	
40	50	10	0.58	3.03	2.97	1.987	2.295	0.0012	0.0027	1.81	43.7
			0.03	0.23		0.005	0.004			0.79	
40	60	0	0.56	3.16	2.84	1.998	2.297	0.0012	0.0027	2.27	43.6
			0.03	0.23		0.006	0.005			0.80	
50	5	45	0.65	2.80	3.20	2.001	2.302	0.0012	0.0027	2.22	39.74
			0.02	0.20		0.006	0.004			0.73	
50	10	40	0.63	3.22	2.78	2.001	2.300	0.0012	0.0027	1.67	37.69
			0.02	0.19		0.005	0.004			0.67	
50	**20**	**30**	**0.58**	**3.03**	**2.97**	**1.993**	**2.293**	**0.0012**	**0.0027**	**1.25**	**32.8**
			0.03			0.004	0.004	0.0005	0.0004	0.61	
50	30	20	0.58	3.01	2.99	1.996	2.297	0.0012	0.0027	1.70	36.68
			0.02	0.18		0.005	0.004			0.65	
50	40	10	0.56	2.99	3.01	1.992	2.297	0.0012	0.0027	1.63	35
			0.02	0.17		0.004	0.003			0.62	
50	50	0	0.57	3.05	2.95	1.992	2.298	0.0012	0.0027	1.52	36.32
			0.02	0.18		0.004	0.004			0.64	
60	20	20	0.58	2.90	3.10	2.010	2.303	0.0012	0.0027	2.33	35.27
			0.02	0.18		0.005	0.004			0.65	
60	30	10	0.58	3.02	2.98	1.997	2.299	0.0012	0.0027	1.65	34.22
			0.02	0.17		0.004	0.003			0.60	
60	40	0	0.57	3.04	2.96	2.010	2.303	0.0012	0.0027	3.08	46.4
			0.03	0.25		0.007	0.005			0.88	
70	20	10	0.60	2.87	3.13	2.009	2.304	0.0012	0.0027	1.92	32.6
			0.02	0.16		0.005	0.003			0.59	
70	30	0	0.57	2.97	3.03	2.006	2.302	0.0012	0.0027	1.80	38.35
			0.02	0.19		0.005	0.004			0.70	

Table S2: The corresponding Pearson's r values for each of the correlations in fig. S1 are presented.

	ρ (g/cm^3)	A_1	A_1/A_2	σ (mS/cm)	$c_{\mathrm{Cl^-,complex}}$ (mol/L)	$WN_{\widehat{HOH}}$ (cm^{-1})
$c_{\mathrm{Cr^{3+}}}$	0.9868	0.9307	-0.1115	-0.2018	0.8951	-0.9857
$c_{\mathrm{Ch^+}}$	-0.4193	-0.2302	0.8044	-0.6448	-0.1385	0.5845
$c_{\mathrm{Cl^-,tot}}$	0.9289	0.9767	0.3559	-0.6347	0.9898	-0.7627
$c_{\mathrm{Cl^-,complex}}$	0.9468	0.9952	0.2965	-0.5371	1.0000	-0.8183
$c_{\mathrm{Cl^-,free}}$	-0.8678	-0.9110	-0.0617	0.1443	-0.8883	0.8414
$c_{\mathrm{H_2O,tot}}$	0.1892	-0.0115	-0.8760	0.7867	-0.1049	-0.4133
$c_{\mathrm{H_2O,added}}$	-0.4388	-0.6064	-0.8173	0.9269	-0.6784	0.1217
$c_{\mathrm{H_2O,complex}}$	0.8436	0.7025	-0.4631	0.1406	0.6365	-0.9069
$c_{\mathrm{H_2O,free}}$	-0.1479	-0.3348	-0.8855	0.9208	-0.4216	-0.1399
$N_{\mathrm{H_2O}}$	-0.3029	-0.4004	-0.9209	0.8625	-0.5564	-0.0664
$c_{\mathrm{Cl^-}}/c_{\mathrm{H_2O}}$	0.1292	0.2102	0.9914	-0.7169	0.3892	-0.1300
$x_{\mathrm{H_2O,added}}$	-0.5354	-0.6698	-0.7484	0.6757	-0.7588	0.4072

Table S3: An overview the 37 different sample compositions of the DES-water mixtures is given in the first three columns. The remaining five columns indicate which techniques were used on these samples.

mol% $CrCl_3 \cdot 6\,H_2O$	mol% ChCl	mol% H_2O	Density	UV/Vis	EXAFS	Conductivity	ATR-FTIR
0	0	100	x			x	x
0	10	90	x			x	x
0	20	80	x			x	x
0	30	70	x			x	x
5	0	95	x	x	x	x	x
5	10	85	x	x	x	x	x
5	20	75	x	x	x	x	x
5	30	65	x	x	x	x	x
5	40	55	x	x	x	x	x
5	50	45		x	x		x
10	0	90	x	x	x	x	x
10	10	80	x	x	x	x	x
10	20	70	x	x	x	x	x
10	30	60	x	x	x	x	x
10	40	50	x	x	x	x	x
10	50	40	x	x	x	x	x
20	10	70	x	x	x	x	x
20	20	60	x	x	x	x	x
20	30	50	x	x	x	x	x
20	40	40	x	x	x	x	x
20	50	30	x	x	x	x	x
20	60	20	x	x	x	x	x
20	70	10	x	x	x	x	x
30	20	50		x	x	x	x
30	30	40	x	x	x	x	x
30	40	30	x	x	x	x	x
30	50	20	x	x	x	x	x
30	60	10	x	x	x	x	x
30	70	0	x	x	x	x	x
40	30	30	x	x	x	x	x
40	40	20	x	x	x	x	x
40	50	10	x	x	x	x	x
40	60	0	x	x	x	x	x
50	30	20	x	x	x	x	
50	40	10	x	x	x	x	
50	50	0	x	x	x	x	x
60	40	0	x	x	x	x	

S3 Correction equations for samples outside the boundary conditions

From the second part of the main paper, it is clear that various equations can be used to calculate a large range of concentrations of important components in the DES-water mixtures. However, for samples outside the boundary conditions (red stars and triangles), the calculations appear to be less reliable. Fortunately, some corrections can be applied in order to improve the accuracy of the calculations for these less concentrated samples. It should be clear that these corrections are only necessary for samples which are outside the boundary conditions.

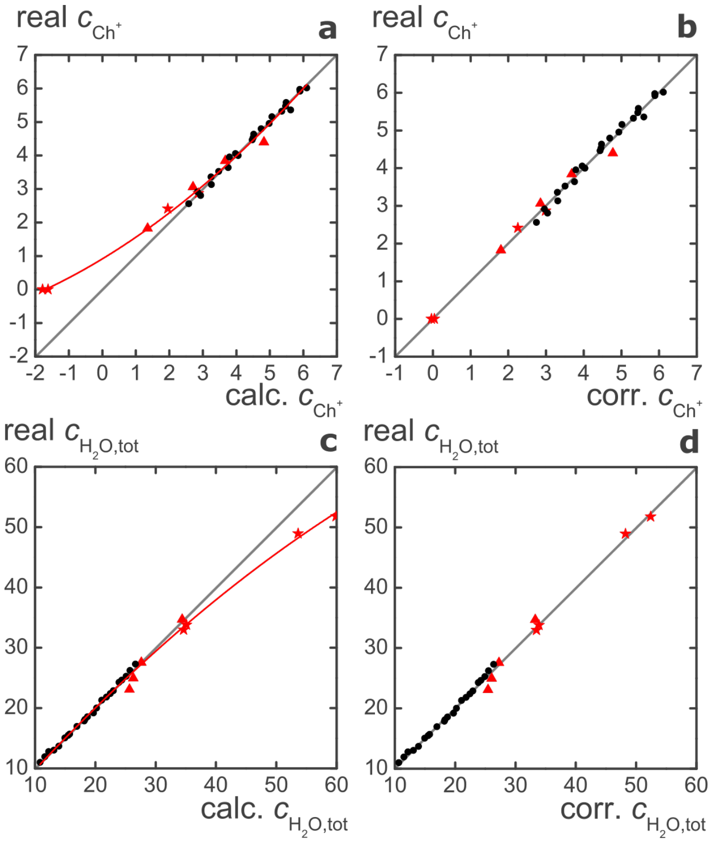


Figure S11: In (a) and (c), polynomial fits were used to correct for the deviations from linearity for the compositions outside the boundary conditions. The adjusted R^2-values were 0.99109 (a) and 0.995 (c). In this way, corrected equations are obtained for c_{Ch^+} and $c_{\mathrm{H_2O,tot}}$. The corrected concentrations are compared with the real values in (b) and (d) respectively. All concentrations are given in mol/L.

A correction function is obtained in order to improve the accuracy of c_{Ch^+} for the diluted conditions. This was done by fitting a polynomial through the data points representing the real concentration of the choline cation as a function of the calculated concentration (fig. S11a):

$$c_{\mathrm{Ch}^+}^{\mathrm{corrected}}(\mathrm{mol/L}) = 0.04026c_{\mathrm{Ch}^+}^2 + 0.60616c_{\mathrm{Ch}^+} + 0.91528 \tag{S1}$$

As can be seen in fig. S11b, strongly improved results for the stars and triangles are obtained in comparison with the uncorrected calculation (fig. 13g in the main paper). However, it should still be kept in mind that this equation can only be used for standard DES-water mixtures and not for electrolytes during or after electroplating.

In addition, the deviation present in the calculation of $c_{\mathrm{H_2O,tot}}$ (fig. 9h in the main paper) can again be corrected for by a second order polynomial:

$$c_{\mathrm{H_2O,tot}}^{\mathrm{corrected}}(\mathrm{mol/L}) = -0.00426c_{\mathrm{H_2O,tot}}^2 + 1.15224c_{\mathrm{H_2O,tot}} - 1.31469 \tag{S2}$$

Which is illustrated in fig. S11c. These improved results cannot only be used for the calculation of $c_{\mathrm{H_2O,tot}}$, but also to improve the calculations of most of the concentrations that were described above.

Firstly, a corrected function of the concentration of coordinating water ligands can be obtained by subtracting the con-

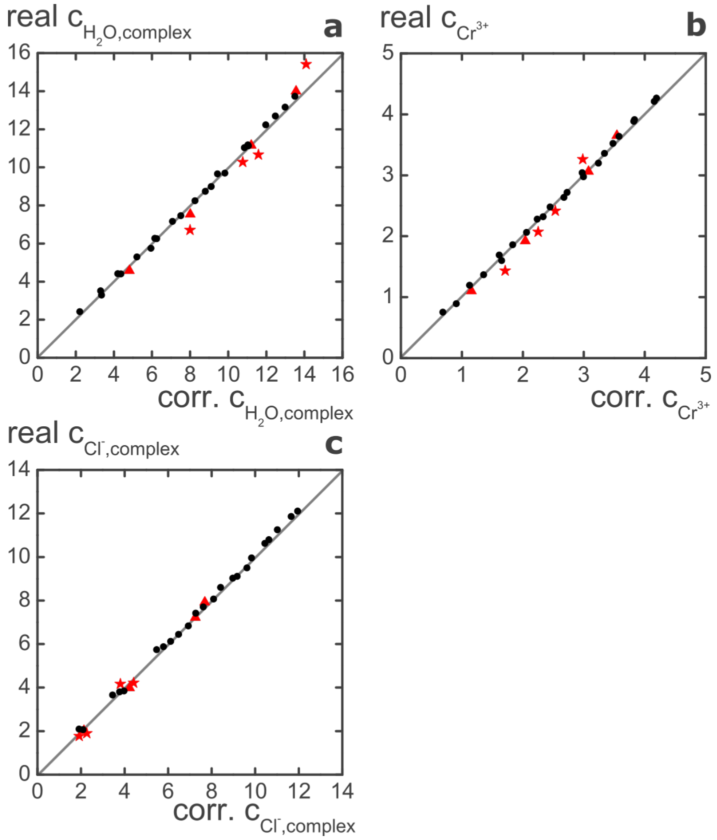


Figure S12: The corrections obtained in fig. S11 and eq. S1 and S2, can also be used to construct improved equations for (a) $c_{\mathrm{H_2O,complex}}$ (eq. S3), (b) $c_{\mathrm{Cr^{3+}}}$ (eq. S4), and (c) $c_{\mathrm{Cl^-,complex}}$ (eq. S5). All concentrations are in mol/L. Comparison of (a), (b), and (c) with fig. 11d, c, and b (main paper) respectively, shows that large improvements can be made for the DES-water compositions outside the boundary conditions, when using the corrected equations.

centration of 'free' water $c_{\mathrm{H_2O,free}}$ from the corrected concentration of the total water $c^{\mathrm{corrected}}_{\mathrm{H_2O,tot}}$:

$$\begin{aligned} c^{\mathrm{corrected}}_{\mathrm{H_2O,complex}}(\mathrm{mol/L}) &= c^{\mathrm{corrected}}_{\mathrm{H_2O,tot}} - c_{\mathrm{H_2O,free}} \\ &= c^{\mathrm{corrected}}_{\mathrm{H_2O,tot}} - \frac{1}{0.1119\left(\frac{A_1}{A_2}\right)^2 - 0.15181} \end{aligned} \tag{S3}$$

$c^{\mathrm{corrected}}_{\mathrm{H_2O,complex}}$ is compared with the real concentration of coordinating water in fig. S12a.
It was not necessary to find a corrected function for $c_{\mathrm{H_2O,free}}$, because good results can already be obtained for all data points by eq. 14 (main paper). Additionally, corrected functions for the concentration of Cr(III) $c^{\mathrm{corrected}}_{\mathrm{Cr^{3+}}}$ and the concentration of coordinating chloride anions $c^{\mathrm{corrected}}_{\mathrm{Cl^-,complex}}$ can be obtained in a similar fashion:

$$\begin{aligned} c^{\mathrm{corrected}}_{\mathrm{Cr^{3+}}}(\mathrm{mol/L}) &= \frac{c^{\mathrm{corrected}}_{\mathrm{H_2O,complex}}}{N_{\mathrm{H_2O}}} \\ &= \frac{c^{\mathrm{corrected}}_{\mathrm{H_2O,tot}} - \frac{1}{0.1119\left(\frac{A_1}{A_2}\right)^2 - 0.15181}}{-0.0470\lambda_1 + 25.2155} \end{aligned} \tag{S4}$$

$$\begin{aligned} c^{\mathrm{corrected}}_{\mathrm{Cl^-,complex}}(\mathrm{mol/L}) &= c^{\mathrm{corrected}}_{\mathrm{Cr^{3+}}} \cdot N_{\mathrm{Cl^-}} \\ &= \left(\frac{0.0470\lambda_1 - 19.2155}{-0.0470\lambda_1 + 25.2155}\right) \cdot \left(c^{\mathrm{corrected}}_{\mathrm{H_2O,tot}} - \frac{1}{0.1119\left(\frac{A_1}{A_2}\right)^2 - 0.15181}\right) \end{aligned} \tag{S5}$$

These corrected concentrations are validated with respect to the real values in fig. S12b and c. When comparing fig. S12a, b and c to the corresponding plots in fig. 11d, c, and b (main paper) respectively, it is observed that the corrected equations result in major improvements for the compositions represented by the red stars and triangles.

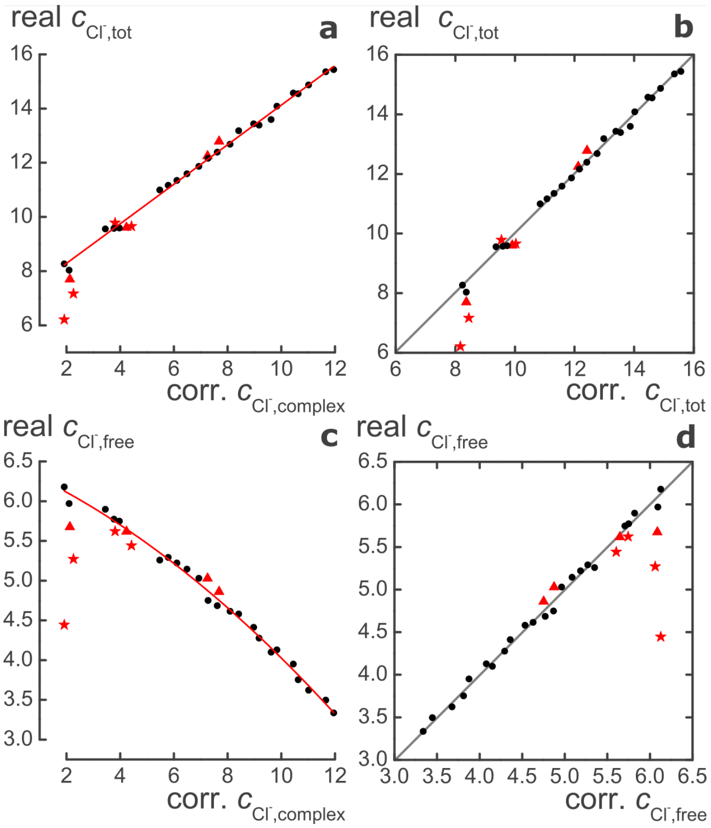


Figure S13: The corrections obtained in fig. S13 and eq. S1 and S2, can also be used to construct improved equations, based on the corrected concentration of coordinating chlorides. In (a), the fit for $c_{\mathrm{Cl^-,tot}}$ was based on the compositions within the boundary conditions and resulted in an adjusted R^2 of 0.99614 (eq. S6). Similarly, in the case of $c_{\mathrm{Cl^-,free}}$, the polynomial fit with the compositions within the boundary conditions, resulted in eq. S7 and an adjusted R^2-value of 0.9936. The corresponding plots which compare the real concentrations with the calculated values after correction, are shown in (b) and (d). Comparing with fig. 13f and c (main paper), shows that slight improvements can be made for the samples outside the boundary conditions, by using the corrected equations. However, the improvements are much less pronounced than in fig. S12. All concentrations are in mol/L.

Finally, from the correlation plot (fig. S1), it is observed that both $c_{\mathrm{Cl^-,tot}}$ and $c_{\mathrm{Cl^-,free}}$ are correlated reasonably well with $c_{\mathrm{Cl^-,complex}}$. Hence $c^{\mathrm{corrected}}_{\mathrm{Cl^-,tot}}$ can be used to construct corrected equations for the total and 'free' concentration of chlorides. The fits in fig. S13a and c result in the following equations:

$$\begin{aligned} c^{\mathrm{corrected}}_{\mathrm{Cl^-,tot}}(\mathrm{mol/L}) &= 0.73008 c^{\mathrm{corrected}}_{\mathrm{Cl^-,complex}} + 6.82668 \\ &= 0.73008 \left(\frac{0.0470\lambda_1 - 19.2155}{-0.0470\lambda_1 + 25.2155} \right) \cdot \left(c^{\mathrm{corrected}}_{\mathrm{H_2O,tot}} - \frac{1}{0.1119 \left(\frac{A_1}{A_2} \right)^2 - 0.15181} \right) + 6.82668 \end{aligned} \tag{S6}$$

$$c^{\mathrm{corrected}}_{\mathrm{Cl^-,free}}(\mathrm{mol/L}) = -0.00918 \left(c^{\mathrm{corrected}}_{\mathrm{Cl^-,complex}} \right)^2 - 0.15065 c^{\mathrm{corrected}}_{\mathrm{Cl^-,complex}} + 6.45069 \tag{S7}$$

However, comparing fig. S13b and d with the corresponding uncorrected plots in fig. 13f and d, shows that certainly for $c^{\mathrm{corrected}}_{\mathrm{Cl^-,free}}$, but also for $c^{\mathrm{corrected}}_{\mathrm{Cl^-,tot}}$, only minor improvements are made. Hence, one should still be careful using these equations if the compositions are outside the boundary conditions.

S4 Fitting reports

$$\sigma(\mathrm{mS/cm}) = 0.05686 \cdot c^2_{\mathrm{H_2O,added}} \tag{7}$$

Parameters

		Value	Standard Error	t-Value	Prob>|t|	Dependency
conductivity	B2	0.05686	0.00117	48.80462	0	0

Reduced Chi-sqr = 5.16869001601
COD(R^2) = 0.98502358525775
Iterations Performed = 3
Total Iterations in Session = 3
Fit converged. Chi-Sqr tolerance value of 1E-9 was reached.
Standard Error was scaled with square root of reduced Chi-Sqr.
Some input data points are missing.

Statistics

	conductivity
Number of Points	31
Degrees of Freedom	30
Reduced Chi-Sqr	5.16869
Residual Sum of Squares	155.0607
R-Square(COD)	0.98502
Adj. R-Square	0.98502
Fit Status	Succeeded(100)

Fit Status Code :
100 : Fit converged. Chi-Sqr tolerance value of 1E-9 was reached

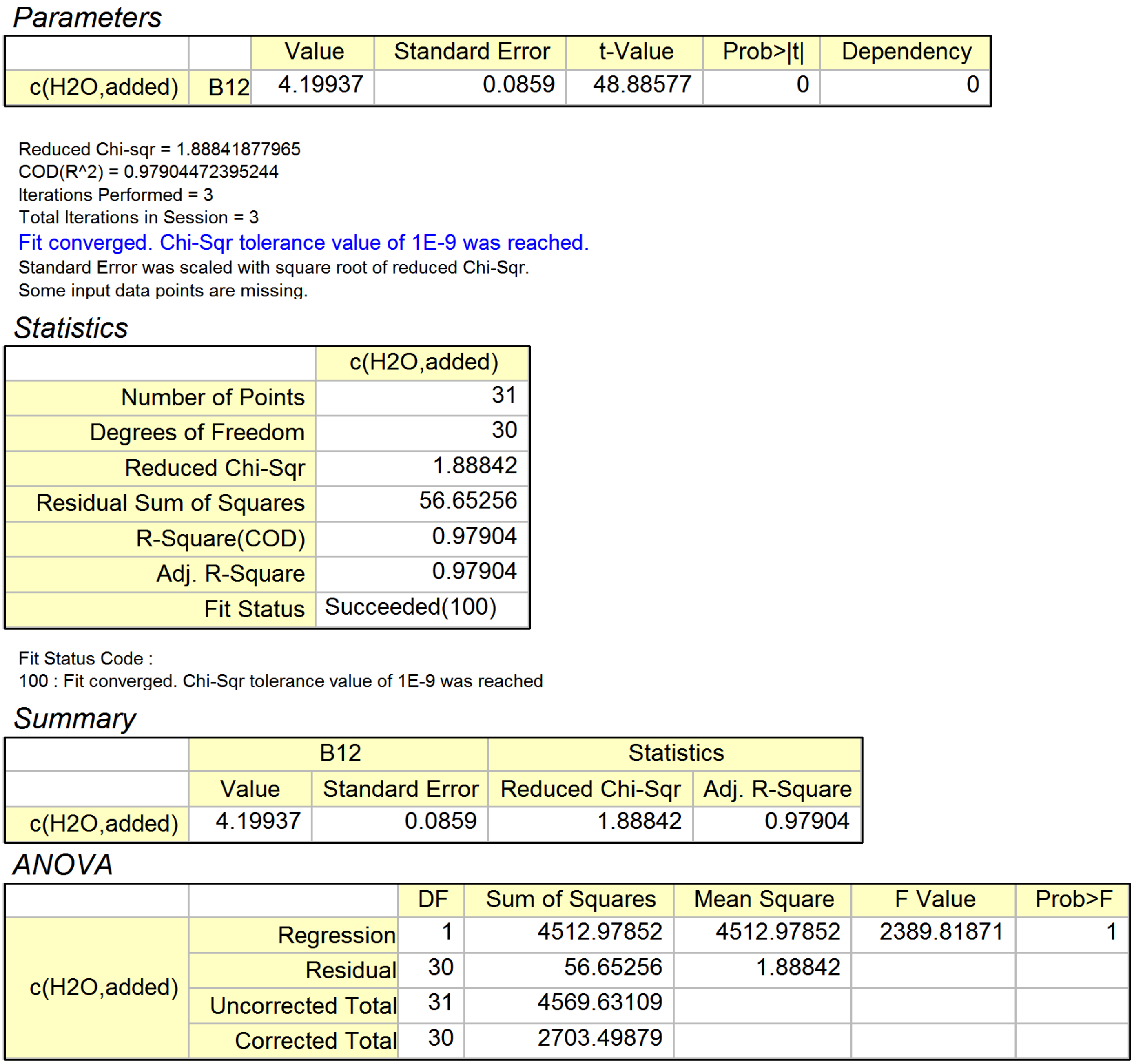
Summary

	B2		Statistics	
	Value	Standard Error	Reduced Chi-Sqr	Adj. R-Square
conductivity	0.05686	0.00117	5.16869	0.98502

ANOVA

		DF	Sum of Squares	Mean Square	F Value	Prob>F
conductivity	Regression	1	12311.25649	12311.25649	2381.89105	1
	Residual	30	155.0607	5.16869		
	Uncorrected Total	31	12466.31719			
	Corrected Total	30	10353.65961			

$$c_{\mathrm{H_2O,added}}(\mathrm{mol/L}) = 4.19937 \cdot \sqrt{\sigma} \tag{8}$$



Parameters

		Value	Standard Error	t-Value	Prob>|t|	Dependency
c(H2O,added)	B12	4.19937	0.0859	48.88577	0	0

Reduced Chi-sqr = 1.88841877965
COD(R^2) = 0.97904472395244
Iterations Performed = 3
Total Iterations in Session = 3
Fit converged. Chi-Sqr tolerance value of 1E-9 was reached.
Standard Error was scaled with square root of reduced Chi-Sqr.
Some input data points are missing.

Statistics

	c(H2O,added)
Number of Points	31
Degrees of Freedom	30
Reduced Chi-Sqr	1.88842
Residual Sum of Squares	56.65256
R-Square(COD)	0.97904
Adj. R-Square	0.97904
Fit Status	Succeeded(100)

Fit Status Code :
100 : Fit converged. Chi-Sqr tolerance value of 1E-9 was reached

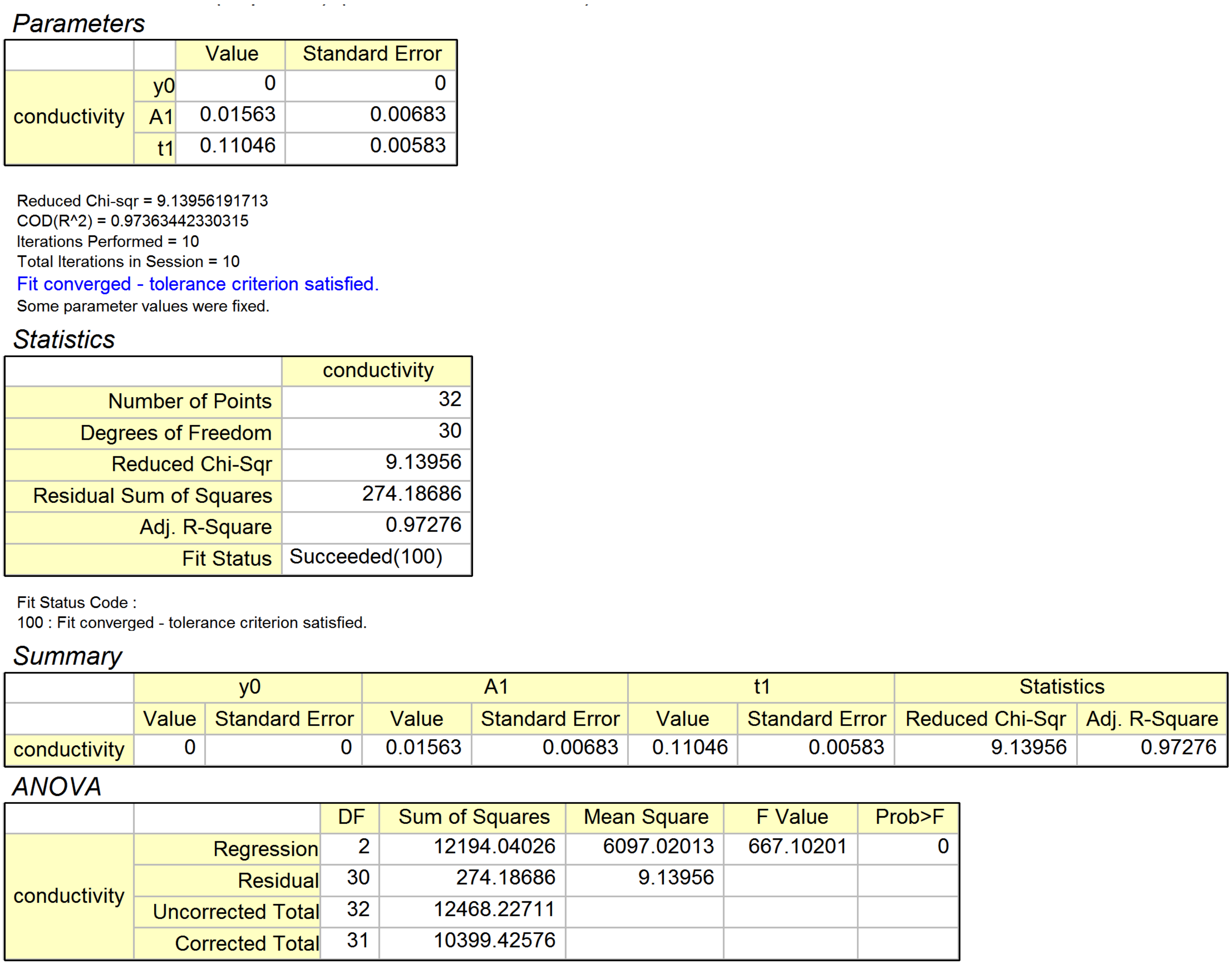
Summary

	B12		Statistics	
	Value	Standard Error	Reduced Chi-Sqr	Adj. R-Square
c(H2O,added)	4.19937	0.0859	1.88842	0.97904

ANOVA

		DF	Sum of Squares	Mean Square	F Value	Prob>F
c(H2O,added)	Regression	1	4512.97852	4512.97852	2389.81871	1
	Residual	30	56.65256	1.88842		
	Uncorrected Total	31	4569.63109			
	Corrected Total	30	2703.49879			

$$\sigma(\mathrm{mS/cm}) = 0.01563 \cdot e^{\frac{x_{\mathrm{H_2O,added}}}{0.11046}} \tag{9}$$



Parameters

		Value	Standard Error
conductivity	y0	0	0
	A1	0.01563	0.00683
	t1	0.11046	0.00583

Reduced Chi-sqr = 9.13956191713
COD(R^2) = 0.97363442330315
Iterations Performed = 10
Total Iterations in Session = 10
Fit converged - tolerance criterion satisfied.
Some parameter values were fixed.

Statistics

	conductivity
Number of Points	32
Degrees of Freedom	30
Reduced Chi-Sqr	9.13956
Residual Sum of Squares	274.18686
Adj. R-Square	0.97276
Fit Status	Succeeded(100)

Fit Status Code :
100 : Fit converged - tolerance criterion satisfied.

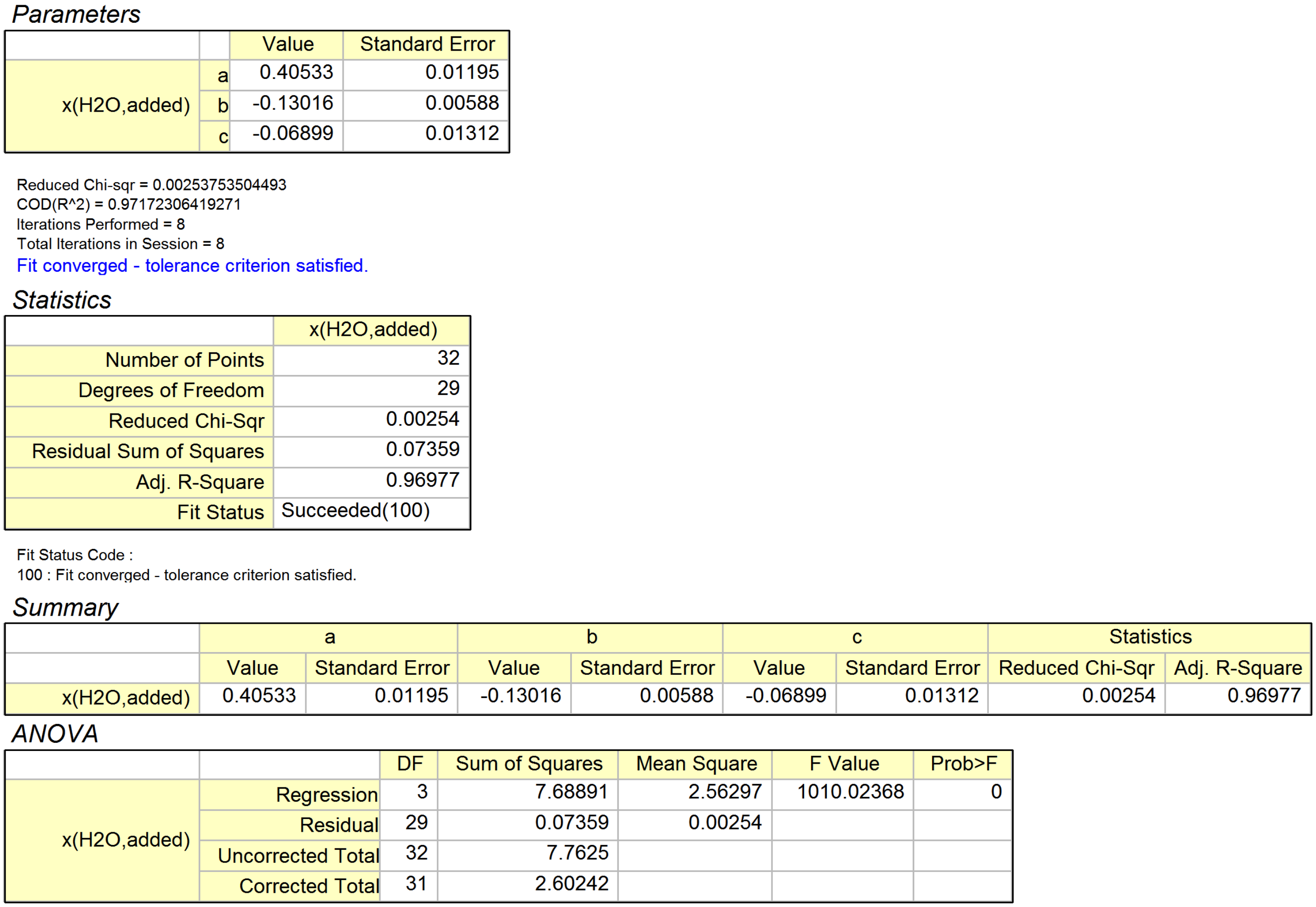
Summary

	y0		A1		t1		Statistics	
	Value	Standard Error	Value	Standard Error	Value	Standard Error	Reduced Chi-Sqr	Adj. R-Square
conductivity	0	0	0.01563	0.00683	0.11046	0.00583	9.13956	0.97276

ANOVA

		DF	Sum of Squares	Mean Square	F Value	Prob>F
conductivity	Regression	2	12194.04026	6097.02013	667.10201	0
	Residual	30	274.18686	9.13956		
	Uncorrected Total	32	12468.22711			
	Corrected Total	31	10399.42576			

$$x_{\mathrm{H_2O,added}} = 0.13016 \cdot ln(\sigma - 0.06899) + 0.40533 \tag{10}$$



Parameters

		Value	Standard Error
x(H2O,added)	a	0.40533	0.01195
	b	-0.13016	0.00588
	c	-0.06899	0.01312

Reduced Chi-sqr = 0.00253753504493
COD(R^2) = 0.97172306419271
Iterations Performed = 8
Total Iterations in Session = 8
Fit converged - tolerance criterion satisfied.

Statistics

	x(H2O,added)
Number of Points	32
Degrees of Freedom	29
Reduced Chi-Sqr	0.00254
Residual Sum of Squares	0.07359
Adj. R-Square	0.96977
Fit Status	Succeeded(100)

Fit Status Code :
100 : Fit converged - tolerance criterion satisfied.

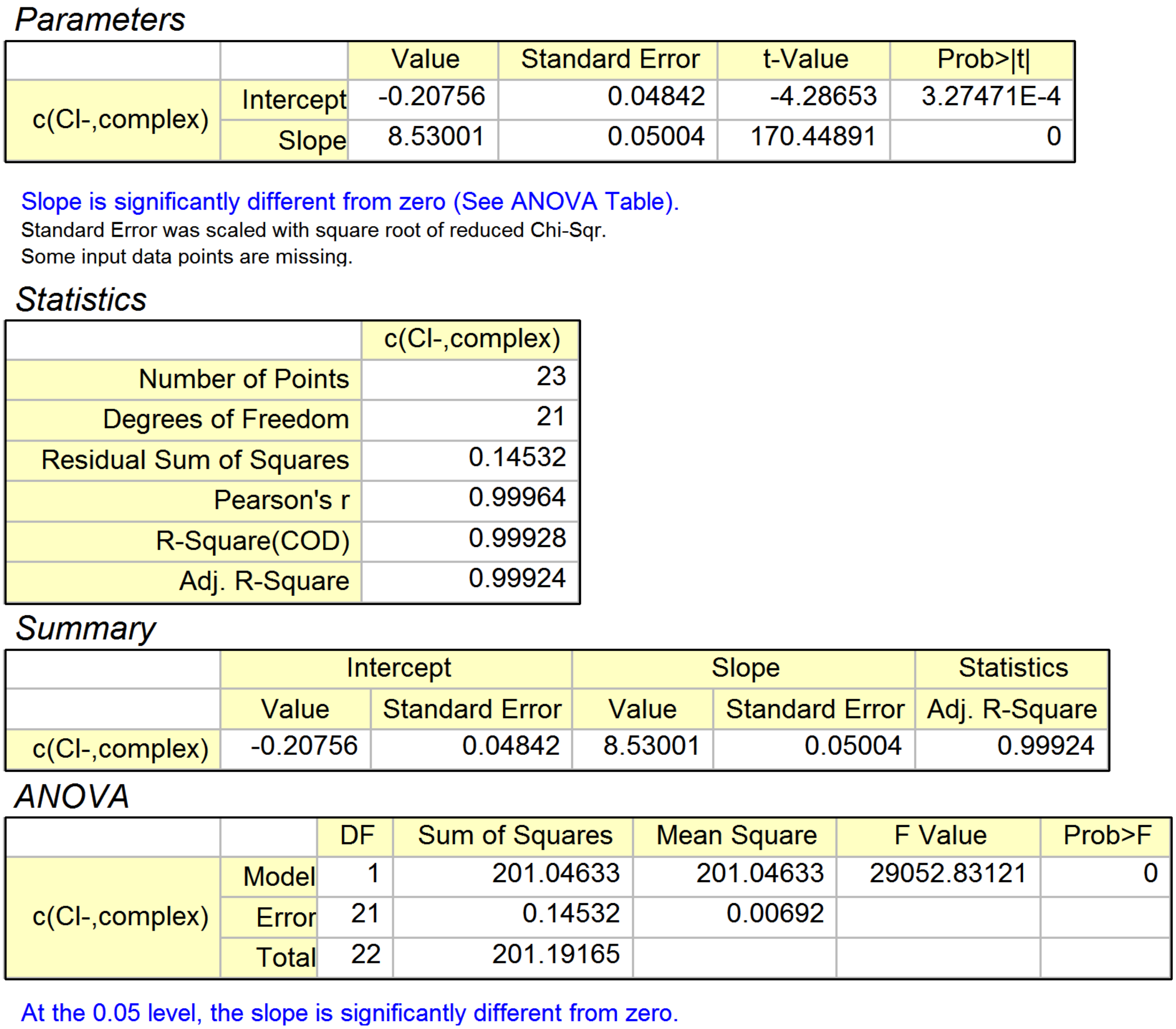
Summary

	a		b		c		Statistics	
	Value	Standard Error	Value	Standard Error	Value	Standard Error	Reduced Chi-Sqr	Adj. R-Square
x(H2O,added)	0.40533	0.01195	-0.13016	0.00588	-0.06899	0.01312	0.00254	0.96977

ANOVA

		DF	Sum of Squares	Mean Square	F Value	Prob>F
x(H2O,added)	Regression	3	7.68891	2.56297	1010.02368	0
	Residual	29	0.07359	0.00254		
	Uncorrected Total	32	7.7625			
	Corrected Total	31	2.60242			

$$c_{\mathrm{Cl^-,complex}}(\mathrm{mol/L}) = 8.53001A_1 - 0.20756 \tag{11}$$



Parameters

		Value	Standard Error	t-Value	Prob>|t|
c(Cl-,complex)	Intercept	-0.20756	0.04842	-4.28653	3.27471E-4
	Slope	8.53001	0.05004	170.44891	0

Slope is significantly different from zero (See ANOVA Table).
Standard Error was scaled with square root of reduced Chi-Sqr.
Some input data points are missing.

Statistics

	c(Cl-,complex)
Number of Points	23
Degrees of Freedom	21
Residual Sum of Squares	0.14532
Pearson's r	0.99964
R-Square(COD)	0.99928
Adj. R-Square	0.99924

Summary

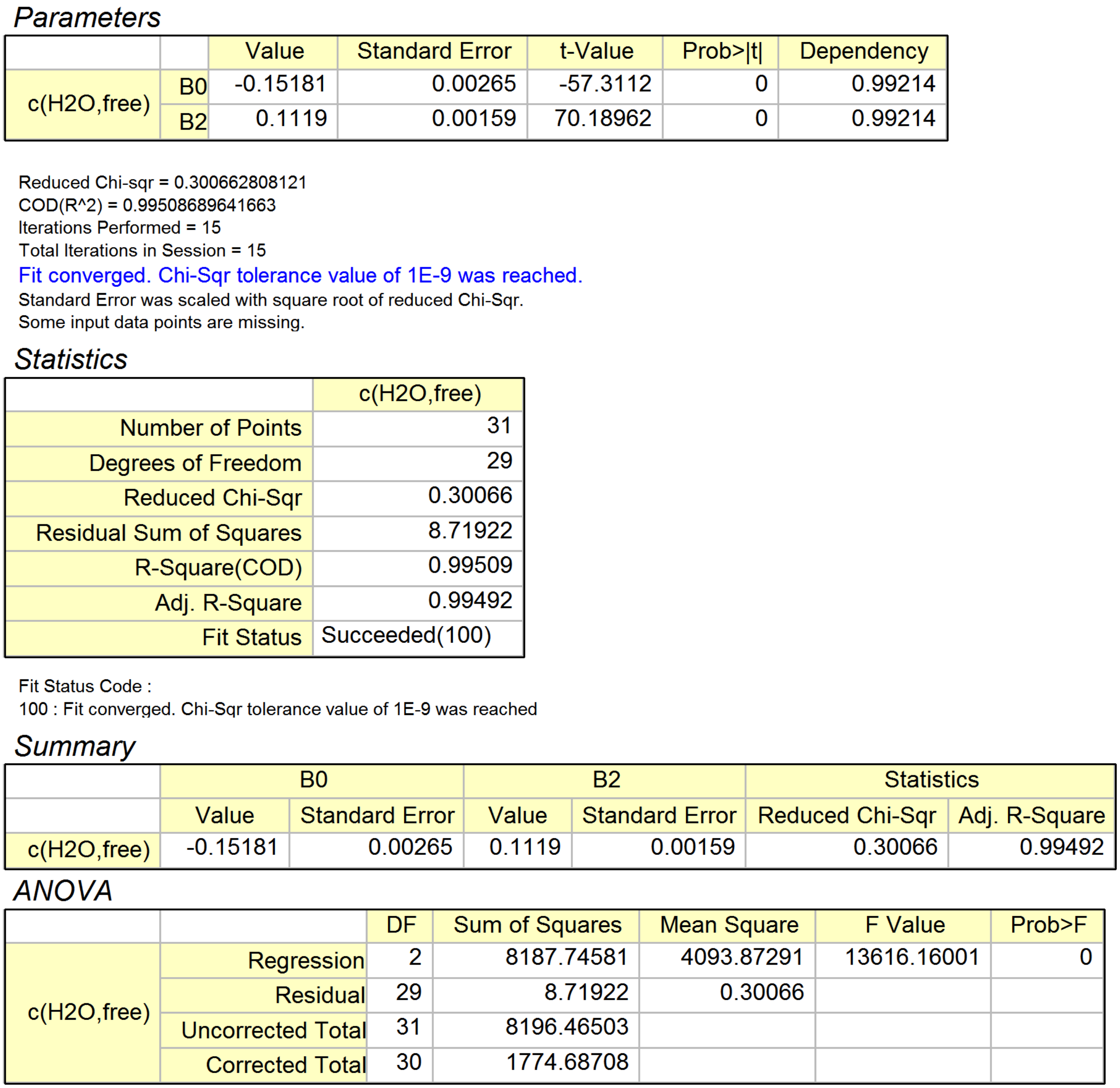
	Intercept		Slope		Statistics
	Value	Standard Error	Value	Standard Error	Adj. R-Square
c(Cl-,complex)	-0.20756	0.04842	8.53001	0.05004	0.99924

ANOVA

		DF	Sum of Squares	Mean Square	F Value	Prob>F
c(Cl-,complex)	Model	1	201.04633	201.04633	29052.83121	0
	Error	21	0.14532	0.00692		
	Total	22	201.19165			

At the 0.05 level, the slope is significantly different from zero.

$$c_{\mathrm{H_2O,free}}(\mathrm{mol/L}) = \frac{1}{0.1119\left(\frac{A_1}{A_2}\right)^2 - 0.15181} \tag{14}$$



Parameters

		Value	Standard Error	t-Value	Prob>|t|	Dependency
c(H2O,free)	B0	-0.15181	0.00265	-57.3112	0	0.99214
	B2	0.1119	0.00159	70.18962	0	0.99214

Reduced Chi-sqr = 0.300662808121
COD(R^2) = 0.99508689641663
Iterations Performed = 15
Total Iterations in Session = 15
Fit converged. Chi-Sqr tolerance value of 1E-9 was reached.
Standard Error was scaled with square root of reduced Chi-Sqr.
Some input data points are missing.

Statistics

	c(H2O,free)
Number of Points	31
Degrees of Freedom	29
Reduced Chi-Sqr	0.30066
Residual Sum of Squares	8.71922
R-Square(COD)	0.99509
Adj. R-Square	0.99492
Fit Status	Succeeded(100)

Fit Status Code :
100 : Fit converged. Chi-Sqr tolerance value of 1E-9 was reached

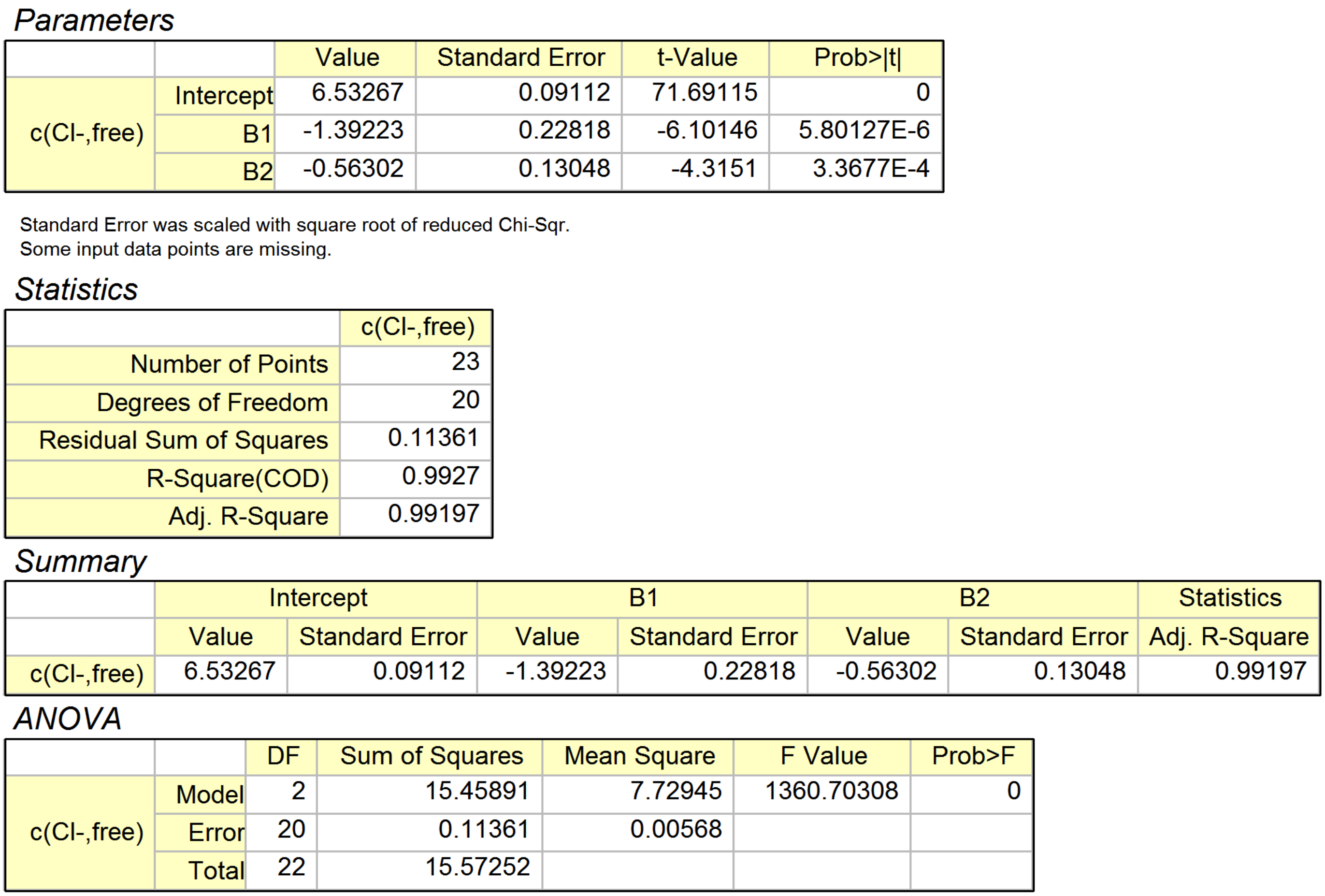
Summary

	B0		B2		Statistics	
	Value	Standard Error	Value	Standard Error	Reduced Chi-Sqr	Adj. R-Square
c(H2O,free)	-0.15181	0.00265	0.1119	0.00159	0.30066	0.99492

ANOVA

		DF	Sum of Squares	Mean Square	F Value	Prob>F
c(H2O,free)	Regression	2	8187.74581	4093.87291	13616.16001	0
	Residual	29	8.71922	0.30066		
	Uncorrected Total	31	8196.46503			
	Corrected Total	30	1774.68708			

$$c_{\mathrm{Cl^-,free}}(\mathrm{mol/L}) = -0.56302A_1^2 - 1.39223A_1 + 6.53267 \tag{15}$$



Parameters

		Value	Standard Error	t-Value	Prob>|t|
c(Cl-,free)	Intercept	6.53267	0.09112	71.69115	0
	B1	-1.39223	0.22818	-6.10146	5.80127E-6
	B2	-0.56302	0.13048	-4.3151	3.3677E-4

Standard Error was scaled with square root of reduced Chi-Sqr.
Some input data points are missing.

Statistics

	c(Cl-,free)
Number of Points	23
Degrees of Freedom	20
Residual Sum of Squares	0.11361
R-Square(COD)	0.9927
Adj. R-Square	0.99197

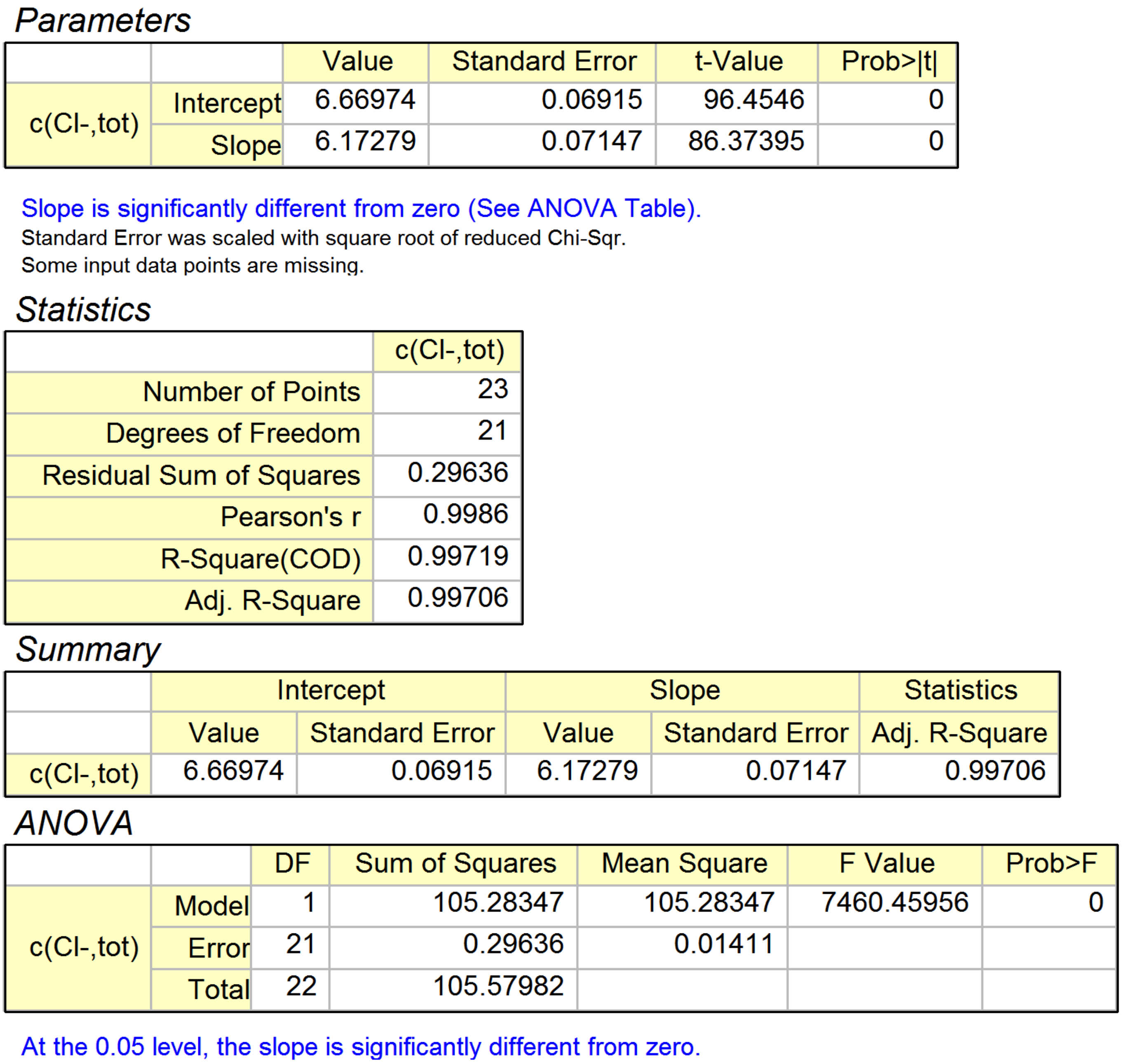
Summary

	Intercept		B1		B2		Statistics
	Value	Standard Error	Value	Standard Error	Value	Standard Error	Adj. R-Square
c(Cl-,free)	6.53267	0.09112	-1.39223	0.22818	-0.56302	0.13048	0.99197

ANOVA

		DF	Sum of Squares	Mean Square	F Value	Prob>F
c(Cl-,free)	Model	2	15.45891	7.72945	1360.70308	0
	Error	20	0.11361	0.00568		
	Total	22	15.57252			

$$c_{\mathrm{Cl^-,tot}}(\mathrm{mol/L}) = 6.17279A_1 + 6.66974 \tag{16}$$



Parameters

		Value	Standard Error	t-Value	Prob>|t|
c(Cl-,tot)	Intercept	6.66974	0.06915	96.4546	0
	Slope	6.17279	0.07147	86.37395	0

Slope is significantly different from zero (See ANOVA Table).

Standard Error was scaled with square root of reduced Chi-Sqr.

Some input data points are missing.

Statistics

	c(Cl-,tot)
Number of Points	23
Degrees of Freedom	21
Residual Sum of Squares	0.29636
Pearson's r	0.9986
R-Square(COD)	0.99719
Adj. R-Square	0.99706

Summary

	Intercept		Slope		Statistics
	Value	Standard Error	Value	Standard Error	Adj. R-Square
c(Cl-,tot)	6.66974	0.06915	6.17279	0.07147	0.99706

ANOVA

		DF	Sum of Squares	Mean Square	F Value	Prob>F
c(Cl-,tot)	Model	1	105.28347	105.28347	7460.45956	0
	Error	21	0.29636	0.01411		
	Total	22	105.57982			

At the 0.05 level, the slope is significantly different from zero.

$$c_{\mathrm{Ch^+}}^{\mathrm{corrected}}(\mathrm{mol/L}) = 0.04026c_{\mathrm{Ch^+}}^2 - 0.60616c_{\mathrm{Ch^+}} + 0.91528 \tag{S1}$$

Parameters

		Value	Standard Error	t-Value	Prob>|t|
real c(Ch+)	Intercept	0.91528	0.0586	15.61872	2.44249E-15
	B1	0.60616	0.02853	21.24619	0
	B2	0.04026	0.00514	7.84009	1.53654E-8

Standard Error was scaled with square root of reduced Chi-Sqr.
Some input data points are missing.

Statistics

	real c(Ch+)
Number of Points	31
Degrees of Freedom	28
Residual Sum of Squares	0.59103
R-Square(COD)	0.99168
Adj. R-Square	0.99109

Summary

	Intercept		B1		B2		Statistics
	Value	Standard Error	Value	Standard Error	Value	Standard Error	Adj. R-Square
real c(Ch+)	0.91528	0.0586	0.60616	0.02853	0.04026	0.00514	0.99109

ANOVA

		DF	Sum of Squares	Mean Square	F Value	Prob>F
real c(Ch+)	Model	2	70.46356	35.23178	1669.10977	0
	Error	28	0.59103	0.02111		
	Total	30	71.05459			

$$c_{\mathrm{H_2O,tot}}^{\mathrm{corrected}}(\mathrm{mol/L}) = -0.00426c_{\mathrm{H_2O,tot}}^{2} + 1.15224c_{\mathrm{H_2O,tot}} - 1.31469 \tag{S2}$$

Parameters

		Value	Standard Error	t-Value	Prob>|t|
real c(H2O,tot)	Intercept	-1.31469	0.68774	-1.91161	0.06621
	B1	1.15224	0.04769	24.16114	0
	B2	-0.00426	6.98998E-4	-6.10049	1.39711E-6

Standard Error was scaled with square root of reduced Chi-Sqr.
Some input data points are missing.

Statistics

	real c(H2O,tot)
Number of Points	31
Degrees of Freedom	28
Residual Sum of Squares	12.97022
R-Square(COD)	0.99534
Adj. R-Square	0.995

Summary

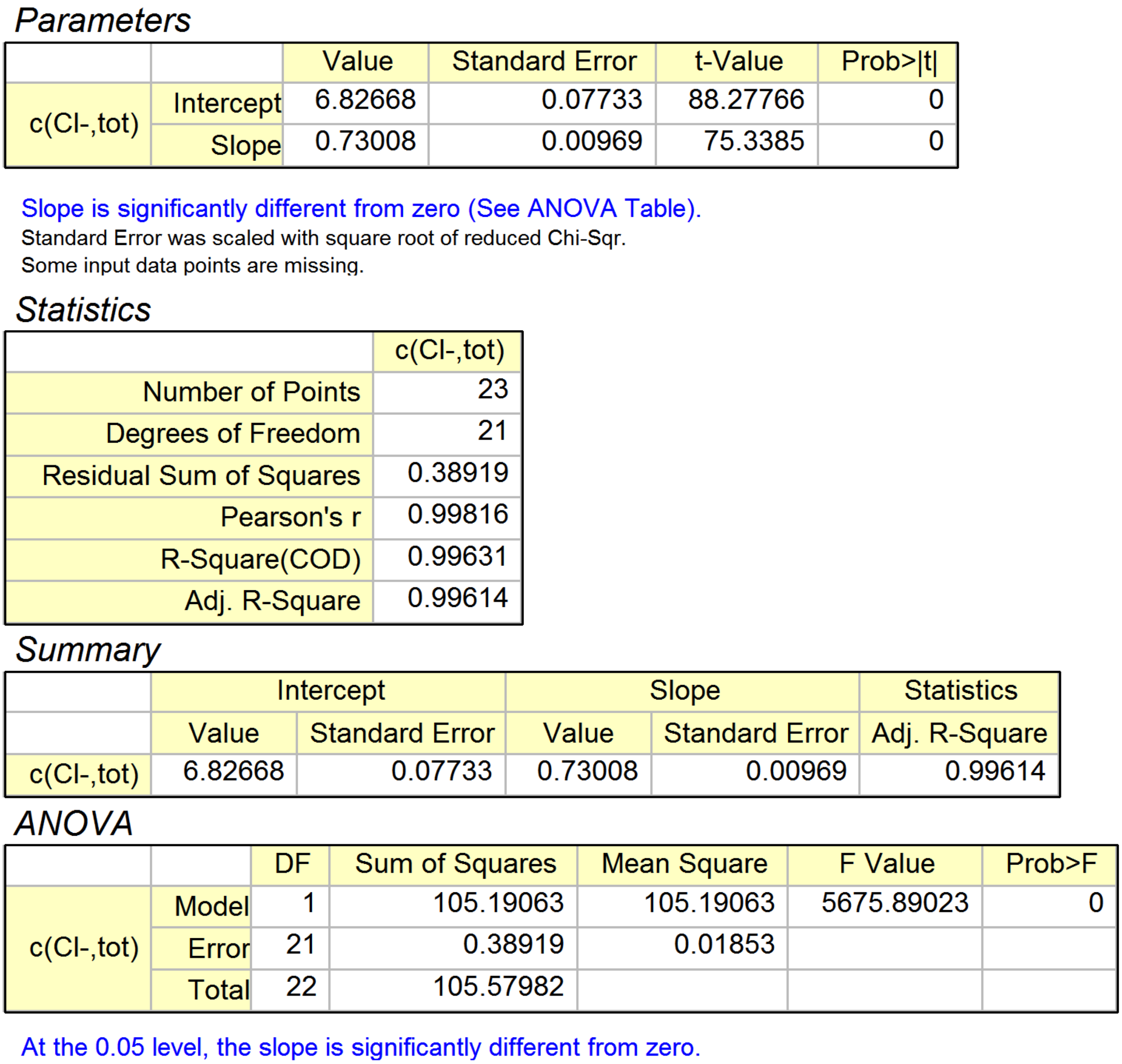
	Intercept		B1		B2		Statistics
	Value	Standard Error	Value	Standard Error	Value	Standard Error	Adj. R-Square
real c(H2O,tot)	-1.31469	0.68774	1.15224	0.04769	-0.00426	6.98998E-4	0.995

ANOVA

		DF	Sum of Squares	Mean Square	F Value	Prob>F
real c(H2O,tot)	Model	2	2768.41906	1384.20953	2988.21895	0
	Error	28	12.97022	0.46322		
	Total	30	2781.38929			

$$c^{\text{corrected}}_{\text{Cl}^-,\text{tot}}(\text{mol/L}) = 0.73008 c_{\text{Cl}^-,\text{tot}} + 6.82668$$

$$= 0.73008 \left(\frac{0.0470\lambda_1 - 19.2155}{-0.0470\lambda_1 + 25.2155} \right) \cdot \left(c^{\text{corrected}}_{\text{H}_2\text{O},\text{tot}} - \frac{1}{0.1119 \left(\frac{A_1}{A_2} \right)^2 - 0.15181} \right) + 6.82668 \tag{S6}$$



Parameters

		Value	Standard Error	t-Value	Prob>|t|
c(Cl-,tot)	Intercept	6.82668	0.07733	88.27766	0
	Slope	0.73008	0.00969	75.3385	0

Slope is significantly different from zero (See ANOVA Table).

Standard Error was scaled with square root of reduced Chi-Sqr.

Some input data points are missing.

Statistics

	c(Cl-,tot)
Number of Points	23
Degrees of Freedom	21
Residual Sum of Squares	0.38919
Pearson's r	0.99816
R-Square(COD)	0.99631
Adj. R-Square	0.99614

Summary

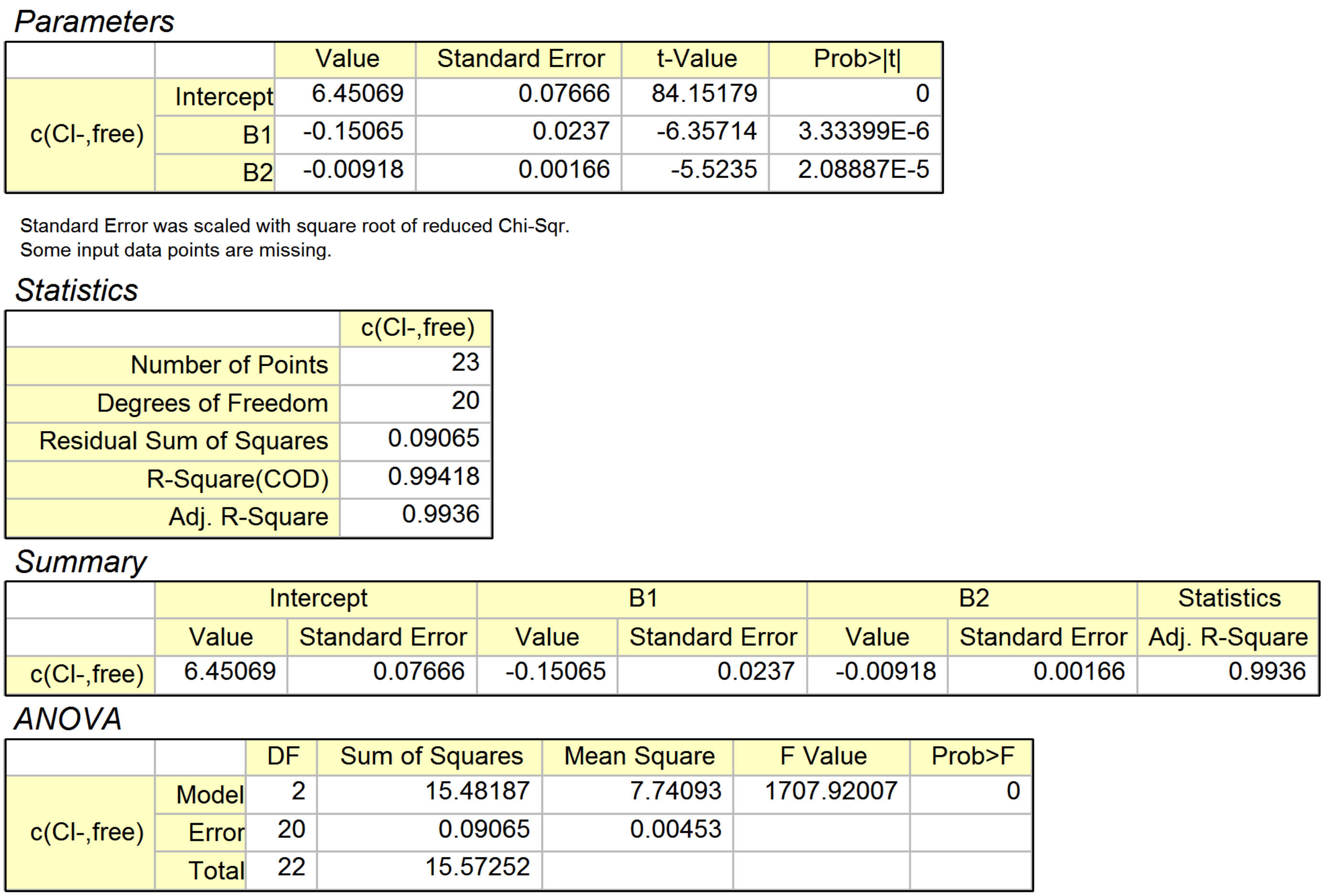
	Intercept		Slope		Statistics
	Value	Standard Error	Value	Standard Error	Adj. R-Square
c(Cl-,tot)	6.82668	0.07733	0.73008	0.00969	0.99614

ANOVA

		DF	Sum of Squares	Mean Square	F Value	Prob>F
c(Cl-,tot)	Model	1	105.19063	105.19063	5675.89023	0
	Error	21	0.38919	0.01853		
	Total	22	105.57982			

At the 0.05 level, the slope is significantly different from zero.

$$c_{\mathrm{Cl^-,free}}^{\mathrm{corrected}}(\mathrm{mol/L}) = -0.00918\left(c_{\mathrm{Cl^-,complex}}^{\mathrm{corrected}}\right)^2 - 0.15065c_{\mathrm{Cl^-,complex}}^{\mathrm{corrected}} + 6.45069 \tag{S7}$$



Parameters

		Value	Standard Error	t-Value	Prob>|t|
c(Cl-,free)	Intercept	6.45069	0.07666	84.15179	0
	B1	-0.15065	0.0237	-6.35714	3.33399E-6
	B2	-0.00918	0.00166	-5.5235	2.08887E-5

Standard Error was scaled with square root of reduced Chi-Sqr.
Some input data points are missing.

Statistics

	c(Cl-,free)
Number of Points	23
Degrees of Freedom	20
Residual Sum of Squares	0.09065
R-Square(COD)	0.99418
Adj. R-Square	0.9936

Summary

	Intercept		B1		B2		Statistics
	Value	Standard Error	Value	Standard Error	Value	Standard Error	Adj. R-Square
c(Cl-,free)	6.45069	0.07666	-0.15065	0.0237	-0.00918	0.00166	0.9936

ANOVA

		DF	Sum of Squares	Mean Square	F Value	Prob>F
c(Cl-,free)	Model	2	15.48187	7.74093	1707.92007	0
	Error	20	0.09065	0.00453		
	Total	22	15.57252			