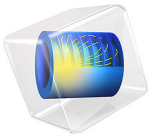

Model created in COMSOL Multiphysics 6.4

Acid-Base Equilibria and Copper Speciation in Ammonia Solution

Introduction

Cupric ions show a strong affinity to ammonia in aqueous solutions, forming strongly colored deep blue complexes. The relative amounts of the different ammine ligand complexes, with varying coordination numbers, are governed by the stability constants of the equilibria forming the coordination compounds. By entering a series of equilibrium reactions, and an external source of ammonia, the Time Dependent study can be used to produce a speciation diagram, which shows how the concentration of the different complexes vary with the total concentration of added ammonia.

Model Definition

A 0D component employing the **Reaction Engineering** interface is used to describe the system. The equilibria for a simplified model is entered as **Reaction** features in the interface. The equilibria used in this model are presented in Table 1, together with approximate equilibrium constants at room temperature, partially derived from Ref. 1.

TABLE 1: EQUILIBRIA GOVERNING THE SPECIATION IN THE MODEL.

Reactants	Products	Equilibrium constant[a]
H2O	H+ + OH-	1.8e-16[M]
NH4+	H+ + NH3	5.5e-10[M]
CuNH3++	NH3 + Cu++	5.0e-05[M]
Cu(NH3)2++	NH3 + CuNH3++	5.0e-05[M]
Cu(NH3)3++	NH3 + Cu(NH3)2++	1.3e-03[M]
Cu(NH3)4++	NH3 + Cu(NH3)3++	6.3e-03[M]
Cu(NH3)5++	NH3 + Cu(NH3)4++	4.0[M]
2 Cu++ + OH- + H2O	Cu2(OH)2++ + H+	45[M^-2]

a. The autoprotolysis constant of water uses an explicit concentration of water rather than the common assumption of setting its activity to one.

No solid phases are accounted for, nor any ionic strength effects. Instead, focus is on initialization and mass conservation. By adding an **Additional Source** feature, a parameter sweep is modeled by setting a constant rate of addition for one or more components, and use the time-dependent solver to adaptively step through the specified range of values. For initial values, a total concentration of copper is given as the initial value of free cupric ions, the bulk density of water gives its concentration, and a small value is assigned to the swept species which represents the initial value of the sweep. Under the **Equilibria** section of the **Initial Values** feature, the **Mass-preserving initialization** functionality is enabled. This tells the

solver to first solve the equilibria, while ignoring any kinetic reactions, in a mass-consistent manner prior to the time-stepping phase, which in turn allows for specifying initial values far from equilibrium. Note that mass-preserving initialization requires all components to be present (that is, larger than zero) for the set of initial values. This is due the initializer working with a log-transformed version of the problem, in which a concentration of zero cannot be represented by a finite number. For this model, this requirement is already fulfilled, but for other models a reasonable amount might be some fraction of what is expected to be produced during the first time step.

Results and Discussion

The evolution of concentrations, as total concentration of ammonia is increased, is presented in Figure 1. As might be expected, ammonia is primarily present as ammonium at low total concentrations of ammonia, and primarily as the free base at high total concentration. In the transition region, when the total concentration of ammonia is similar to the total concentration of copper(II) ions in the system, the picture is more complicated, and ammine complexes of different coordination numbers form.

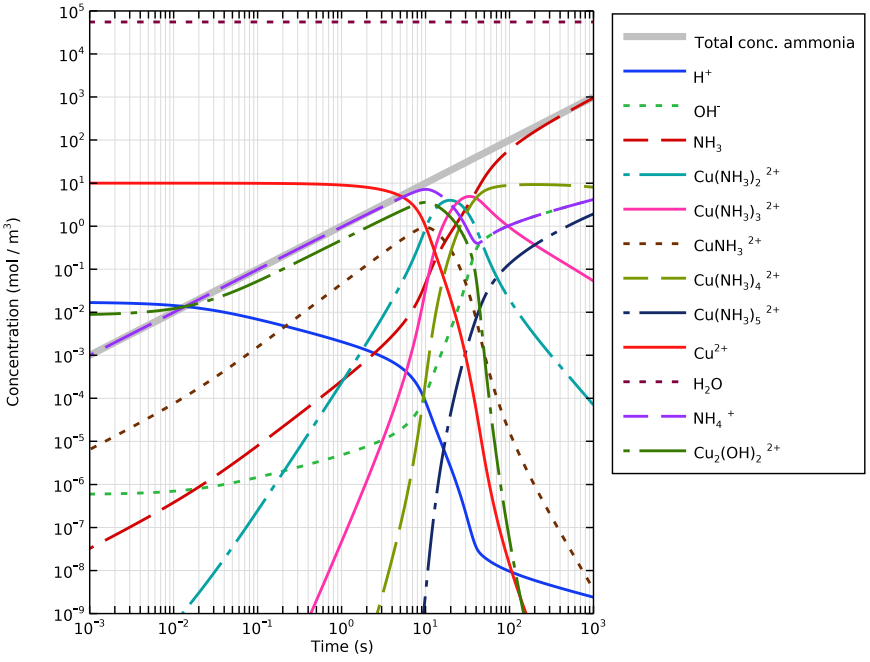

Figure 1: Concentration of species versus time. The constant source of ammonia gives a linear relationship between total concentration ammonia and time.

Since mass-preserving initialization was enabled, it may be interesting to study how the mass conservation is upheld throughout the time stepping. The results for conservation of protons, hydroxide ions, ammonia moieties, and copper are presented in Figure 2.

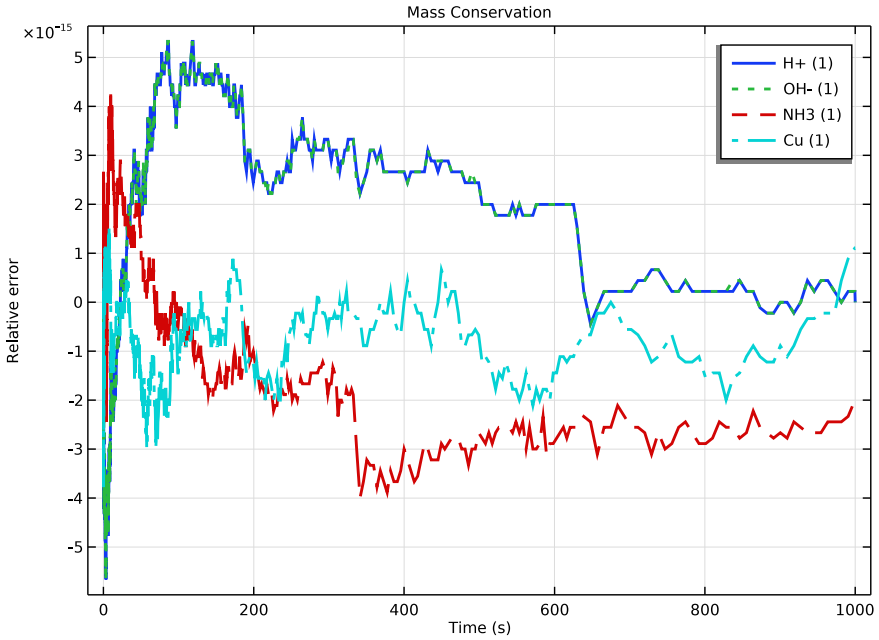

Figure 2: Mass conservation of the constituents in the model. Note that the number of invariants here equal the difference between number of species and equilibria.

An instructive plot can be made over the predominance of the different groups of complexes. By looking at the weighted sum with respect to copper content we can see in Figure 3 how the addition of ammonia alters the speciation of the cupric ion.

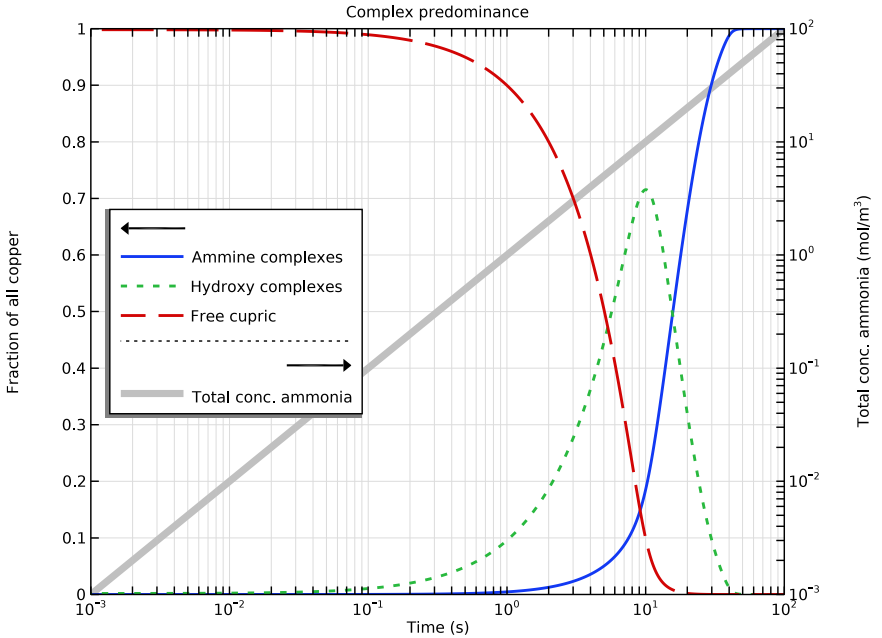

Figure 3: Relative speciation of copper (II) ions into different classes of complexes, and their variation versus total concentration of ammonia.

The early onset of change is due to the basicity ammonia, where the uptake of protons yields a net increase of available hydroxide ion, which forms a binuclear complex of cupric ions with bridging hydroxide. Eventually, as the total availability of ammonia increases, ammine complexes outcompete the hydroxide, yielding a mixture of mononuclear ammines of increasing coordination index as the concentration of ammonia increases.

Reference

1. P. Djurdjevic and others, "Metal Ammine Formation in Solution. XXIV. The Copper (II) — and Some Other Metal (II) — Mono-and Diethanolamine Systems," *Acta. Chem. Scand.*, vol. 37, pp. 881–890, 1983.

Application Library path: `Chemical_Reaction_Engineering_Module/Tutorials/ion_speciation`

Modeling Instructions

From the **File** menu, choose **New**.

NEW

In the **New** window, click **Model Wizard**.

MODEL WIZARD

1 In the **Model Wizard** window, click **0D**.

2 In the **Select Physics** tree, select **Chemical Species Transport** > **Reaction Engineering (re)**.

3 Click **Add**.

4 Click **Study**.

5 In the **Select Study** tree, select **General Studies** > **Time Dependent**.

6 Click **Done**.

REACTION ENGINEERING (RE)

Reaction 1

1 In the **Reaction Engineering** toolbar, click **Reaction**.

2 In the **Settings** window for **Reaction**, locate the **Reaction Formula** section.

3 In the **Formula** text field, type `H2O=H++OH-`.

4 Locate the **Equilibrium Settings** section. In the $K_{\mathrm{eq}0j}$ text field, type `1.80505415e-16[M]`.

Reaction 2

1 In the **Reaction Engineering** toolbar, click **Reaction**.

2 In the **Settings** window for **Reaction**, locate the **Reaction Formula** section.

3 In the **Formula** text field, type `NH4+=H++NH3`.

4 Locate the **Equilibrium Settings** section. In the $K_{\mathrm{eq}0j}$ text field, type `5.49540874e-10[M]`.

Reaction 3

1 In the **Reaction Engineering** toolbar, click **Reaction**.

2 In the **Settings** window for **Reaction**, locate the **Reaction Formula** section.

3 In the **Formula** text field, type `CuNH3++=NH3+Cu++`.

4 Locate the **Equilibrium Settings** section. In the $K_{\mathrm{eq}0j}$ text field, type `5.01187234e-05[M]`.

Reaction 4

1 In the **Reaction Engineering** toolbar, click **Reaction**.

2 In the **Settings** window for **Reaction**, locate the **Reaction Formula** section.

3 In the **Formula** text field, type `Cu(NH3)2++=NH3+CuNH3++`.

4 Locate the **Equilibrium Settings** section. In the $K_{\mathrm{eq}0j}$ text field, type `5.01187234e-05[M]`.

Reaction 5

1 In the **Reaction Engineering** toolbar, click **Reaction**.

2 In the **Settings** window for **Reaction**, locate the **Reaction Formula** section.

3 In the **Formula** text field, type `Cu(NH3)3++=NH3+Cu(NH3)2++`.

4 Locate the **Equilibrium Settings** section. In the $K_{\mathrm{eq}0j}$ text field, type `0.00125893[M]`.

Reaction 6

1 In the **Reaction Engineering** toolbar, click **Reaction**.

2 In the **Settings** window for **Reaction**, locate the **Reaction Formula** section.

3 In the **Formula** text field, type `Cu(NH3)4++=NH3+Cu(NH3)3++`.

4 Locate the **Equilibrium Settings** section. In the $K_{\mathrm{eq}0j}$ text field, type `0.00630957[M]`.

Reaction 7

1 In the **Reaction Engineering** toolbar, click **Reaction**.

2 In the **Settings** window for **Reaction**, locate the **Reaction Formula** section.

3 In the **Formula** text field, type `Cu(NH3)5++=NH3+Cu(NH3)4++`.

4 Locate the **Equilibrium Settings** section. In the $K_{\mathrm{eq}0j}$ text field, type `3.98107171[M]`.

Reaction 8

1 In the **Reaction Engineering** toolbar, click **Reaction**.

2 In the **Settings** window for **Reaction**, locate the **Reaction Formula** section.

3 In the **Formula** text field, type `2Cu++ + OH- + H2O = Cu2(OH)2++ + H+`.

4 Locate the **Equilibrium Settings** section. In the K_{eq0j} text field, type `45.34091032[M^-2]`.

DEFINITIONS

Variables 1

In the **Model Builder** window, under **Component 1 (comp1)** right-click **Definitions** and choose **Variables**.

GLOBAL DEFINITIONS

Parameters 1

1 In the **Settings** window for **Parameters**, locate the **Parameters** section.

2 In the table, enter the following settings:

Name	Expression	Value	Description
init_conc_H2O	55.4[M]	55400 mol/m³	From density and molar mass
init_conc_Cu	0.01[M]	10 mol/m³	Initial concentration copper
init_conc_NH3	1e-12[M]	1E-9 mol/m³	Initial concentration ammonia
src_rate_NH3	1e-3[M/s]	1 mol/(m³·s)	Rate of [NH3] addition
t0	init_conc_NH3/src_rate_NH3	1E-9 s	First output time
final_conc_NH3	1[M]	1000 mol/m³	Final total concentration ammonia
tend	final_conc_NH3/src_rate_NH3	1000 s	Final output time

DEFINITIONS

Variables 1

1 In the **Model Builder** window, under **Component 1 (comp1)** > **Definitions** click **Variables 1**.

2 In the **Settings** window for **Variables**, locate the **Variables** section.

3 In the table, enter the following settings:

Name	Expression	Unit	Description
c_sum_ammines	re.c_CuNH32_2p+ re.c_CuNH33_2p+ re.c_CuNH34_2p+ re.c_CuNH35_2p+ re.c_CuNH3_2p	mol/m³	Ammine complexes
c_sum_hydroxides	2*re.c_Cu2OH2_2p	mol/m³	Hydroxy complexes
c_sum_Cu_tot	re.c_Cu_2p + c_sum_hydroxides + c_sum_ammines	mol/m³	Total conc. copper
c_sum_NH3_tot	re.c_NH4_1p+ re.c_NH3+ re.c_CuNH3_2p+2* re.c_CuNH32_2p+3* re.c_CuNH33_2p+4* re.c_CuNH34_2p+5* re.c_CuNH35_2p	mol/m³	Total conc. ammonia
c_ref_NH3_tot	init_conc_NH3 + (t-t0)* src_rate_NH3	mol/m³	Total conc. ammonia (ref)
c_sum_H1p_tot	re.c_H_1p+ re.c_NH4_1p+ re.c_H2O	mol/m³	Total conc. protons
c_sum_OH1m_tot	re.c_OH_1m+ re.c_H2O+2* re.c_Cu2OH2_2p	mol/m³	Total conc. hydroxide

REACTION ENGINEERING (RE)

Initial Values 1

1 In the **Model Builder** window, under **Component 1 (comp1)** > **Reaction Engineering (re)** click **Initial Values 1**.

2 In the **Settings** window for **Initial Values**, locate the **Volumetric Species Initial Values** section.

3 In the table, enter the following settings:

Species	Concentration (mol/m^3)
Cu++	init_conc_Cu
H2O	init_conc_H2O
NH3	init_conc_NH3

4 Locate the **Equilibria** section. Select the **Mass-preserving initialization** checkbox.

Additional Source 1

1 In the **Reaction Engineering** toolbar, click **Additional Source**.

2 In the **Settings** window for **Additional Source**, locate the **Additional Rate Expression** section.

3 In the **Volumetric species** table, enter the following settings:

Species	Additional rate expression (mol/(m^3*s))
NH3	`src_rate_NH3`

STUDY 1

Step 1: Time Dependent

1 In the **Model Builder** window, under **Study 1** click **Step 1: Time Dependent**.

2 In the **Settings** window for **Time Dependent**, locate the **Study Settings** section.

3 In the **Output times** text field, type `10^range(log10(t0/1[s]),0.5,log10(tend/1[s]))`.

4 From the **Tolerance** list, choose **User controlled**.

5 In the **Relative tolerance** text field, type `1e-6`.

Solution 1 (sol1)

1 In the **Study** toolbar, click **Show Default Solver**.

2 In the **Model Builder** window, expand the **Solution 1 (sol1)** node, then click **Time-Dependent Solver 1**.

3 In the **Settings** window for **Time-Dependent Solver**, click to expand the **Time Stepping** section.

4 Select the **Initial step** checkbox. In the associated text field, type `0.1*t0`.

5 Find the **Algebraic variable settings** subsection. From the **Consistent initialization** list, choose **Off**.

Thanks to mass-preserving initialization we already have a consistent starting point.

6 In the **Study** toolbar, click **Compute**.

RESULTS

Concentration (re)

1 In the **Settings** window for **1D Plot Group**, click to expand the **Title** section.

2 From the **Title type** list, choose **None**.

3 Locate the **Plot Settings** section.

4 Select the **y-axis label** checkbox. In the associated text field, type `Concentration (mol / m<sup>3</sup>)`.

5 Locate the **Axis** section. Select the **Manual axis limits** checkbox.

6 In the **x minimum** text field, type `1e-3`.

7 In the **x maximum** text field, type `1e3`.

8 In the **y minimum** text field, type `1e-9`.

9 In the **y maximum** text field, type `1e5`.

10 Select the **x-axis log scale** checkbox.

11 Select the **y-axis log scale** checkbox.

12 Locate the **Legend** section. From the **Layout** list, choose **Outside graph axis area**.

Species concentrations

1 In the **Model Builder** window, expand the **Concentration (re)** node, then click **Global 1**.

2 In the **Settings** window for **Global**, type `Species concentrations` in the **Label** text field.

3 Click to expand the **Legends** section. From the **Legends** list, choose **Manual**.

4 In the table, enter the following settings:

Legends
H⁺
OH⁻
NH₃
Cu(NH₃)₂ ²⁺
Cu(NH₃)₃ ²⁺
CuNH₃ ²⁺
Cu(NH₃)₄ ²⁺
Cu(NH₃)₅ ²⁺
Cu²⁺
H₂O
NH₄ ⁺
Cu₂(OH)₂ ²⁺

5 Click to expand the **Coloring and Style** section. Find the **Line style** subsection. From the **Line** list, choose **Cycle**.

6 From the **Color cycle** list, choose **Long**.

7 From the **Width** list, choose **2**.

Concentration (re)

Right-click **Results** > **Concentration (re)** > **Species concentrations** and choose **Global**.

Total conc. ammonia

1 In the **Settings** window for **Global**, type `Total conc. ammonia` in the **Label** text field.

2 Locate the **y-Axis Data** section. Click **Clear Table**.

3 In the table, enter the following settings:

Expression	Unit	Description
`c_sum_NH3_tot`	`mol/m^3`	`Total conc. ammonia`

4 Locate the **Coloring and Style** section. From the **Color** list, choose **Gray**.

5 From the **Width** list, choose **5**.

6 Drag and drop above **Species concentrations**.

7 Locate the **Legends** section. Find the **Include** subsection. Select the **Description** checkbox.

8 Clear the **Expression** checkbox.

This is Figure 1.

9 In the **Concentration (re)** toolbar, click **Plot**.

Evaluation Group 1

In the **Results** toolbar, click **Evaluation Group**.

Relative Conservation Errors

1 Right-click **Evaluation Group 1** and choose **Global Evaluation**.

2 In the **Settings** window for **Global Evaluation**, type `Relative Conservation Errors` in the **Label** text field.

3 Locate the **Expressions** section. Click **Clear Table**.

4 In the table, enter the following settings:

Expression	Unit	Description
`c_sum_H1p_tot/init_conc_H2O-1`	1	H+
`c_sum_OH1m_tot/init_conc_H2O-1`	1	OH-
`c_sum_NH3_tot/c_ref_NH3_tot-1`	1	NH3
`c_sum_Cu_tot/init_conc_Cu-1`	1	Cu

5 In the **Evaluation Group 1** toolbar, click **Evaluate**.

EVALUATION GROUP 1

1 Go to the **Evaluation Group 1** window.

2 Click the **Clear Table** button in the window toolbar.

RESULTS

1 In the **Model Builder** window, click **Relative Conservation Errors**.

2 In the **Evaluation Group 1** toolbar, click **Evaluate**.

3 In the **Settings** window for **Global Evaluation**, click the **Table Graph** button in the window toolbar.

Mass Conservation

1 In the **Model Builder** window, under **Results** click **1D Plot Group 2**.

2 In the **Settings** window for **1D Plot Group**, type `Mass Conservation` in the **Label** text field.

3 Locate the **Title** section. From the **Title type** list, choose **Label**.

4 Locate the **Plot Settings** section.

5 Select the **y-axis label** checkbox. In the associated text field, type `Relative error`.

Table Graph 1

1 In the **Model Builder** window, click **Table Graph 1**.

2 In the **Settings** window for **Table Graph**, locate the **Coloring and Style** section.

3 Find the **Line style** subsection. From the **Line** list, choose **Cycle**.

4 From the **Width** list, choose **2**.

5 Click to expand the **Legends** section. Select the **Show legends** checkbox.

This is Figure 2.

Complex predominance

1 In the **Home** toolbar, click **Add Plot Group** and choose **1D Plot Group**.

2 In the **Settings** window for **1D Plot Group**, type `Complex predominance` in the **Label** text field.

3 Click to expand the **Title** section. From the **Title type** list, choose **Label**.

4 Locate the **Plot Settings** section. Select the **Two y-axes** checkbox.

5 Select the **y-axis label** checkbox. In the associated text field, type `Fraction of all copper`.

6 Locate the **Axis** section. Select the **x-axis log scale** checkbox.

7 Select the **Secondary y-axis log scale** checkbox.

8 Select the **Manual axis limits** checkbox.

9 In the **x minimum** text field, type `1e-3`.

10 In the **x maximum** text field, type `1e2`.

11 In the **y minimum** text field, type `0`.

12 In the **Secondary y minimum** text field, type `1e-3`.

13 In the **Secondary y maximum** text field, type `1e2`.

14 Locate the **Legend** section. From the **Position** list, choose **Middle left**.

Total conc. ammonia

1 Right-click **Complex predominance** and choose **Global**.

2 In the **Settings** window for **Global**, type `Total conc. ammonia` in the **Label** text field.

3 Locate the **y-Axis Data** section. Click **Clear Table**.

4 In the table, enter the following settings:

Expression	Unit	Description
`c_sum_NH3_tot`	`mol/m^3`	`Total conc. ammonia`

5 Locate the **y-Axis** section. Select the **Plot on secondary y-axis** checkbox.

6 Locate the **Coloring and Style** section. From the **Color** list, choose **Gray**.

7 From the **Width** list, choose **5**.

8 Locate the **Legends** section. Find the **Include** subsection. Select the **Description** checkbox.

9 Clear the **Expression** checkbox.

Complex predominance

Right-click **Total conc. ammonia** and choose **Global**.

Complex classes

1 In the **Settings** window for **Global**, type `Complex classes` in the **Label** text field.

2 Locate the **y-Axis Data** section. Click **Clear Table**.

3 In the table, enter the following settings:

Expression	Unit	Description
`c_sum_ammines/c_sum_Cu_tot`	1	`Ammine complexes`

Expression	Unit	Description
c_sum_hydroxides/c_sum_Cu_tot	1	Hydroxy complexes
re.c_Cu_2p/c_sum_Cu_tot	1	Free cupric

4 Locate the **Coloring and Style** section. Find the **Line style** subsection. From the **Line** list, choose **Cycle**.

5 From the **Width** list, choose **2**.

6 Locate the **Legends** section. Find the **Include** subsection. Select the **Description** checkbox.

7 Clear the **Expression** checkbox.

This is Figure 3.

8 In the **Complex predominance** toolbar, click **Plot**.