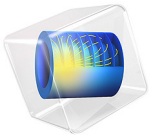


Zone Electrophoresis

Introduction

Zone electrophoresis (ZE) is an electrophoretic separation technique, typically used for analyzing proteins, nucleic acids and biopolymers. During the process different species in a sample are transported in a continuous electrolyte buffer system, subject to a potential gradient. Due to differences in the mobilities, the species in the samples will eventually separate into different, well resolved, peaks.

This tutorial introduces the Electrophoretic Transport interface. A buffer system, consisting of a acetic acid and tris (tris(hydroxymethyl)aminomethane), is used to separate a sample consisting of pyridine and aniline into two well resolved peaks. The model is based on a review paper by Thormann and others (Ref. 1).

Model Definition

The model geometry is represented by an interval in 1D, representing the length (20 cm) of the separation column. The boundaries of the interval is assumed to be facing reservoirs containing large amounts of buffer electrolyte.

The transport of four different species is included: acetic acid, tris, aniline and pyridine. Acetic acid is defined as weak acid, whereas the other species are defined as weak bases. Each species is specified by a mobility and an acid constant (pK_a). For the weak bases the pKa refers to the acid constant of the conjugate acid. Initial and boundary conditions are also specified for each species individually. The initial concentrations for acetic acid and tris are constant over the interval, whereas the sample concentration of aniline and pyridine is defined using a rectangular function with a width of 2.5% of the interval, located close to the leftmost boundary.

In addition to the species concentrations, the Electrophoretic Transport interface also solves for the pH and electrolyte potential distributions. A current density of 2500 A/m^2 is applied at the end of the separation column.

The model is solved using a time-dependent solver, simulating the electrophoresis during 5 minutes.

Results and Discussion

Figures 1 to 4 show the distribution of pH, conductivity, tris and acetic acid at 0 and 4 minutes, respectively. Figure 1, showing the pH, features a rectangular imprint of the initial sample concentrations at 0 minutes, and a more complex distribution pattern at 4 minutes. Figure 2 shows a similar pattern, but with different relative peak heights.

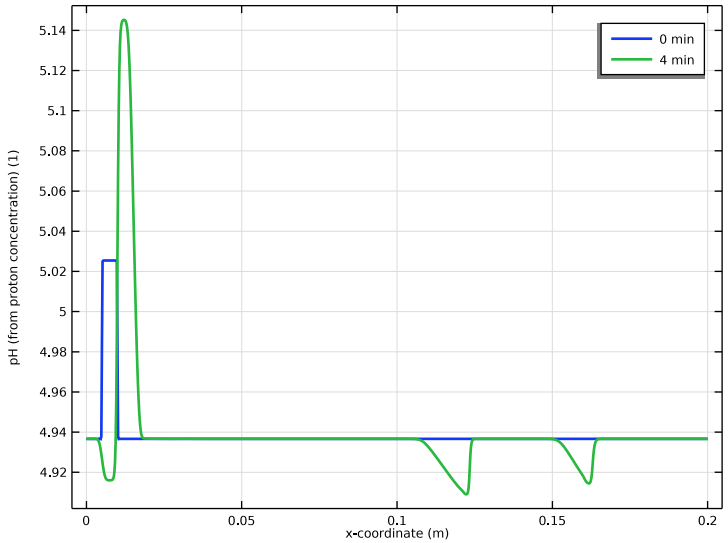


Figure 1: pH distribution at 0 and 4 minutes.

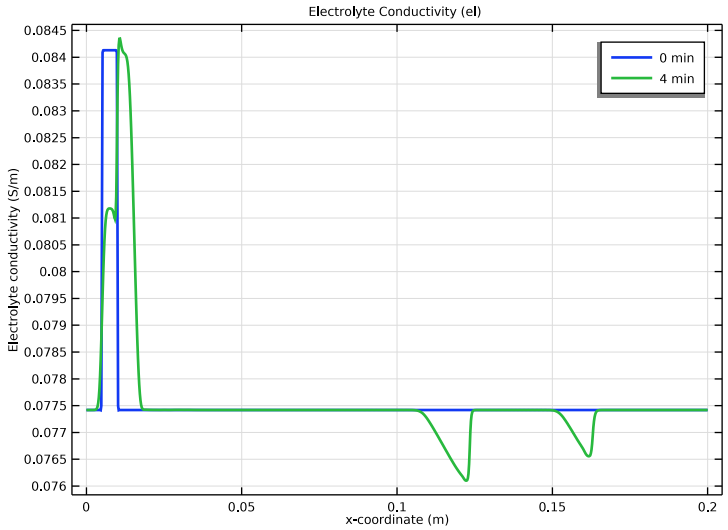


Figure 2: Electrolyte conductivity at 0 and 4 minutes.

Figure 3 and Figure 4 show the concentration distribution of the buffer electrolyte species; tris and acetic acid. Note how the initial position of the sample at $t = 0$ appears as "ghost" peaks in the buffer electrolyte after 4 minutes.

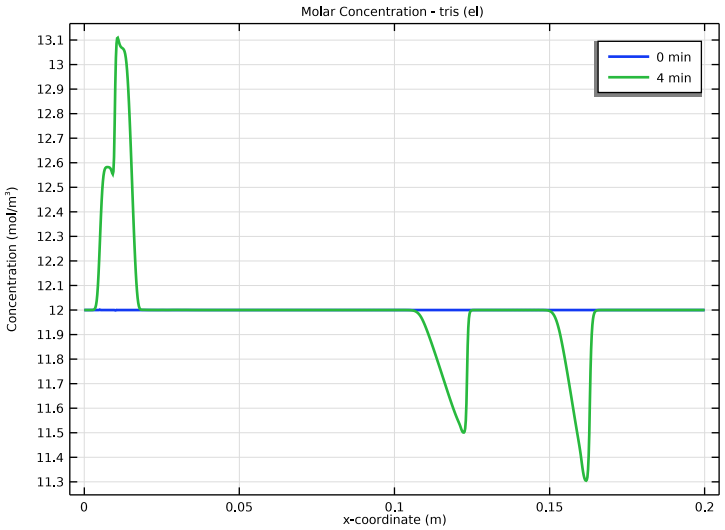


Figure 3: Concentration of tris at 0 and 4 minutes.

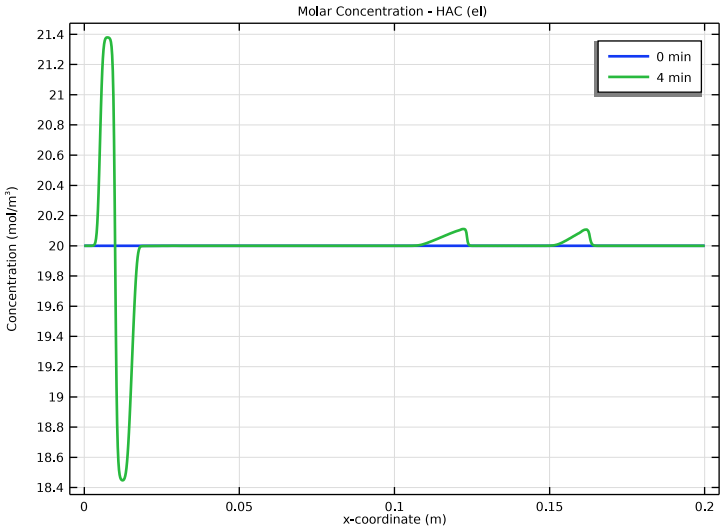


Figure 4: Concentration of acetic acid at 0 and 4 minutes.

Finally, Figure 5 and Figure 6 show the concentration of the pyridine and aniline sample at 1 and 3 minutes. The peaks are shaped as triangles, and the peak-to-peak distance increases as the samples move to the right in the separation column.

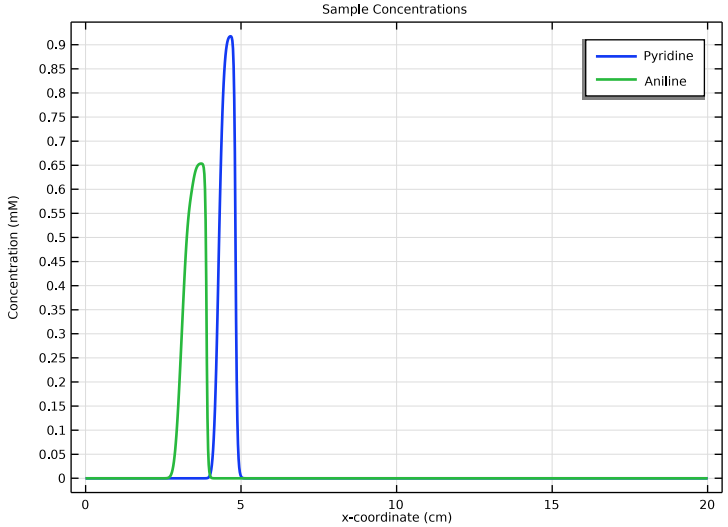


Figure 5: Sample concentrations at 1 min.

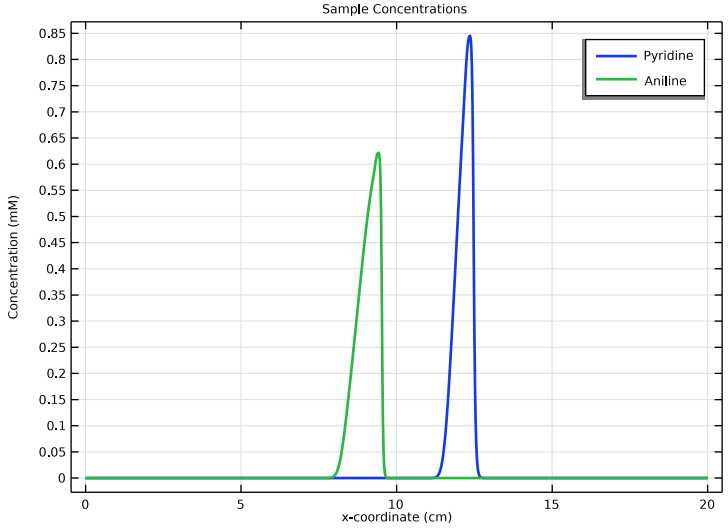


Figure 6: Sample concentrations at 3 min.

Reference

1. W Thormann, M Breadmore, J. Caslavska, and R. Mosher, "Dynamic computer simulations of electrophoresis: A versatile research and teaching tool," *Electrophoresis*, vol. 31, pp. 726–754, 2010.

Application Library path: `Chemical_Reaction_Engineering_Module/Electrokinetic_Effects/zone_electrophoresis`

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 **1D**.

2 In the **Select Physics** tree, select **Chemical Species Transport> Electrophoretic Transport (el)**.

3 Click **Add**.

4 Click **Study**.

5 In the **Select Study** tree, select **Preset Studies for Selected Physics Interfaces> Time Dependent with Initialization**.

6 Click **Done**.

GLOBAL DEFINITIONS

Start by loading some model parameters from a text file.

Parameters 1

1 In the **Model Builder** window, under **Global Definitions** click **Parameters 1**.

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

3 Click **Load from File**.

4 Browse to the model's Application Libraries folder and double-click the file `zone_electrophoresis_parameters.txt`.

The parameter list now contains various parameters, such as `L`, `T`, `mob_HAC`, and so on. These will be used when defining the model.

GEOMETRY 1

Draw the geometry of the model as an interval between 0 and the parameter `L` (=20 cm).

Interval 1 (i1)

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

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

3 In the table, enter the following settings:

Coordinates (m)
0
L

4 Click **Build Selected**.

ELECTROPHORETIC TRANSPORT (EL)

Now start setting up the physics. A number of nodes have already been added by default.

Solvent 1

The **Solvent** node contains various settings relating to the aqueous solvent. Note that the temperature is set later in the **Default Model Inputs** node.

Insulation 1

An **Insulation** has also been created by default. It will later be overridden when you add the boundary conditions for the potential.

Initial Potential 1

If the model does not include potential dependent electrode reactions, the **Initial Potential** does not normally have to be set explicitly. Leave the setting as is.

Weak Base - tris

Now start adding various species nodes to the model. Begin with the weak base of the buffer electrolyte (tris).

1 In the **Model Builder** window, right-click **Electrophoretic Transport (el)** and choose **Weak Base**.

Each species added to the model adds its own equations, solving for a species concentration as the dependent variable. For a species with dissociation steps, the dependent concentration variable refers to the total concentration (the sum of all dissociated subspecies related to the species).

2 In the **Settings** window for **Weak Base**, type `Weak Base - tris` in the **Label** text field.

The **Domain selection** is set to **All domains** by default, so for this model there is no need to change this selection. However, the settings of the selection section can be used to specify that a species should only be present in certain parts of the geometry.

The **Species name**, which has to be unique, determines how the Electrophoretic Transport interface will name a number of variables, such as concentrations and fluxes.

3 Locate the **Weak Base** section. In the **Species name** text field, type `tris`.

The weak base node uses one dissociation reaction by default (**Monoprotic**), specified by one pKa value.

4 In the pK_a text field, type `pKa_tris`.

5 Locate the **Diffusion and Migration** section. In the u_m text field, type `mob_tris`.

Initial Concentration 1

The boundary conditions and the initial values for a species are set by using child nodes.

The **Initial Concentration** node defines the concentration when the simulation starts.

1 In the **Model Builder** window, expand the **Weak Base - tris** node, then click **Initial Concentration 1**.

2 In the **Settings** window for **Initial Concentration**, locate the **Initial Concentration** section.

3 In the c text field, type `tris_c0`.

Weak Base - tris

The **Concentration** node defines the concentration at a boundary, in this case the inlet reservoir.

1 In the **Model Builder** window, click **Weak Base - tris**.

Concentration 1

1 In the **Physics** toolbar, click **Attributes** and choose **Concentration**.

2 Select Boundary 1 only.

3 In the **Settings** window for **Concentration**, locate the **Concentration** section.

4 In the c_0 text field, type `tris_c0`.

Weak Base - tris

The **Outflow** node defines a boundary with zero diffusive flux for the species. This is a suitable condition for at boundaries where the species is transported into a reservoir.

1 In the **Model Builder** window, click **Weak Base - tris**.

Outflow 1

1 In the **Physics** toolbar, click **Attributes** and choose **Outflow**.

2 Select Boundary 2 only.

Weak Acid - HAC

Now proceed similarly to create the weak acid of the buffer electrolyte (HAC).

1 In the **Physics** toolbar, click **Domains** and choose **Weak Acid**.

2 In the **Settings** window for **Weak Acid**, type `Weak Acid - HAC` in the **Label** text field.

3 Locate the **Weak Acid** section. In the **Species name** text field, type `HAC`.

4 In the $\mathrm{p}K_\mathrm{a}$ text field, type `pKa_HAC`.

5 Locate the **Diffusion and Migration** section. In the u_m text field, type `mob_HAC`.

Initial Concentration 1

1 In the **Model Builder** window, expand the **Weak Acid - HAC** node, then click **Initial Concentration 1**.

2 In the **Settings** window for **Initial Concentration**, locate the **Initial Concentration** section.

3 In the c text field, type `HAC_c0`.

Weak Acid - HAC

In the **Model Builder** window, click **Weak Acid - HAC**.

Concentration 1

1 In the **Physics** toolbar, click **Attributes** and choose **Concentration**.

2 Select Boundary 2 only.

3 In the **Settings** window for **Concentration**, locate the **Concentration** section.

4 In the c_0 text field, type `HAC_c0`.

Weak Acid - HAC

In the **Model Builder** window, click **Weak Acid - HAC**.

Outflow 1

1 In the **Physics** toolbar, click **Attributes** and choose **Outflow**.

2 Select Boundary 1 only.

Weak Base - ani

Now start adding the samples (aniline and pyridine) that are to be separated during the zone electrophoresis. A quick way to do this can many times be to duplicate an existing node instead of creating it new from scratch.

1 In the **Model Builder** window, right-click **Weak Base - tris** and choose **Duplicate**.

2 In the **Settings** window for **Weak Base**, type `Weak Base - ani` in the **Label** text field.

3 Locate the **Weak Base** section. In the **Species name** text field, type `ani`.

4 In the $\mathrm{p}K_\mathrm{a}$ text field, type `pKa_ani`.

5 Locate the **Diffusion and Migration** section. In the u_m text field, type `mob_ani`.

DEFINITIONS

Since the initial sample concentrations are not uniform over the whole domain, we need to specify the initial values using functions.

Rectangle 1 (rect1)

1 In the **Model Builder** window, expand the **Weak Base - ani** node.

2 Right-click **Component 1 (comp1)>Definitions** and choose **Functions>Rectangle**.

The rectangle function creates a function between 0 and 1.

3 In the **Settings** window for **Rectangle**, click to expand the **Smoothing** section.

The transition between 0 and 1 is done smoothly instead of using a discrete step. This improves the numerics when solving the problem. Leave the smoothing settings as they are.

Sample function

There are a number of different function types available such as Gaussian Pulse, Interpolation, Step, and so on. Now add a second, **Analytic**, function to finalize the sample function. The function places the rectangle between 2.5% and 5% of the length of the geometry interval.

1 In the **Home** toolbar, click f(x) **Functions** and choose **Global>Analytic**.

2 In the **Settings** window for **Analytic**, type `Sample function` in the **Label** text field.

3 In the **Function name** text field, type `sample`.

4 Locate the **Definition** section. In the **Expression** text field, type `rect1((x-L*0.0375)/(L*0.025))`.

5 Locate the **Units** section. In the table, enter the following settings:

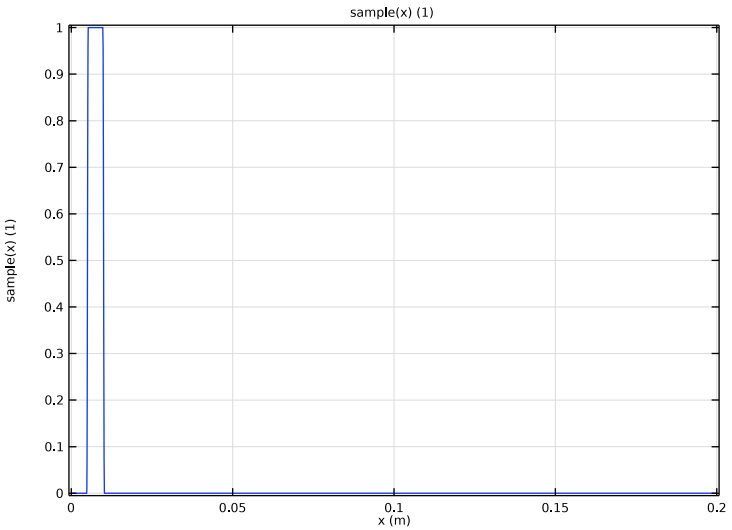
Argument	Unit
x	m

6 In the **Function** text field, type 1.

7 Locate the **Plot Parameters** section. In the table, enter the following settings:

Argument	Lower limit	Upper limit	Unit
x	0	L	m

8 Click **Plot**.



ELECTROPHORETIC TRANSPORT (EL)

Initial Concentration 1

Now use the sample function you just created to define the initial concentration distribution of the aniline species.

1 In the **Model Builder** window, under **Component 1 (comp1)>Electrophoretic Transport (el)>Weak Base - ani** click **Initial Concentration 1**.

2 In the **Settings** window for **Initial Concentration**, locate the **Initial Concentration** section.

3 In the *c* text field, type `sample(x)*ani_c0`.

Concentration 1

1 In the **Model Builder** window, click **Concentration 1**.

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

3 In the c_0 text field, type `0`.

Weak Base - ani

Proceed similarly to create the pyridine species.

Weak Base - pyr

1 In the **Model Builder** window, right-click **Weak Base - ani** and choose **Duplicate**.

2 In the **Settings** window for **Weak Base**, type `Weak Base - pyr` in the **Label** text field.

3 Locate the **Weak Base** section. In the **Species name** text field, type `pyr`.

4 In the pK_a text field, type `pKa_pyr`.

5 Locate the **Diffusion and Migration** section. In the u_m text field, type `mob_pyr`.

Initial Concentration 1

1 In the **Model Builder** window, expand the **Weak Base - pyr** node, then click **Initial Concentration 1**.

2 In the **Settings** window for **Initial Concentration**, locate the **Initial Concentration** section.

3 In the c text field, type `sample(x)*pyr_c0`.

Potential 1

Finally, provide the boundary conditions for the electrolyte potential equation.

1 In the **Physics** toolbar, click **Boundaries** and choose **Potential**.

A potential level always needs defined somewhere in the model, otherwise there will be no unique solution to the problem (which will render a solver error). In this case we will ground the left boundary.

2 Select Boundary 1 only.

Leave the default potential setting value (`0[V]`) as is.

Current Density 1

1 In the **Physics** toolbar, click **Boundaries** and choose **Current Density**.

2 Select Boundary 2 only.

3 In the **Settings** window for **Current Density**, locate the **Electrolyte Current Density** section.

4 In the $i_{n,l}$ text field, type `-2500[A/m^2]`.

Note that we are specifying the value for the current density directly here, instead of using parameters (`L` and so on) as we did before. The brackets `[` and `]` are used to define

the unit. (They may actually be omitted in this case since we are using the same units as the unit system of the model).

GLOBAL DEFINITIONS

Default Model Inputs

Set up the temperature value used in the entire model.

1 In the **Model Builder** window, under **Global Definitions** click **Default Model Inputs**.

2 In the **Settings** window for **Default Model Inputs**, locate the **Browse Model Inputs** section.

3 In the tree, select **General>Temperature (K) - minput.T**.

4 Find the **Expression for remaining selection** subsection. In the **Temperature** text field, type T.

MESH 1

Solve the problem on a mesh consisting of 1000 elements.

1 In the **Model Builder** window, under **Component 1 (comp1)** click **Mesh 1**.

2 In the **Settings** window for **Mesh**, locate the **Sequence Type** section.

3 From the list, choose **User-controlled mesh**.

Distribution 1

1 In the **Model Builder** window, right-click **Edge 1** and choose **Distribution**.

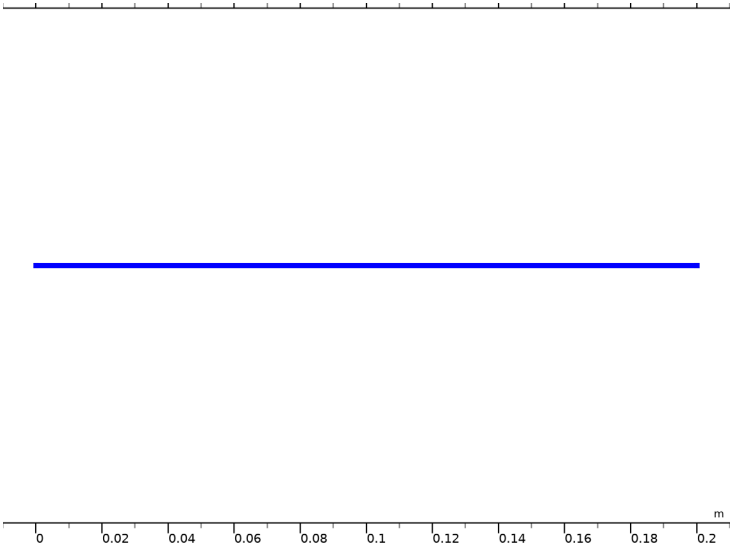
2 In the **Settings** window for **Distribution**, locate the **Distribution** section.

3 In the **Number of elements** text field, type 1000.

Once you have solved the model you can go back and increase the number of elements. This will increase the resolution of the concentration peaks in the solution, but will also increase the computation time.

4 Click **Build All**.

For now, the finalized mesh should now look as follows:



STUDY 1

The problem is now ready for solving. Note that the **Time dependent with Initialization** study you added initially in the model wizard has created a study sequence consisting of one **Current Distribution Initialization** study step followed by one **Time Dependent** step. The initialization step is used to compute the initial potential and pH distribution before the time-dependent solver starts.

Step 2: Time Dependent

Set up the solver to solve between 0 and 5 minutes, storing the solution every 30 s.

1 In the **Model Builder** window, under **Study 1** click **Step 2: Time Dependent**.

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

3 From the **Time unit** list, choose **min**.

4 Click **Range**.

5 In the **Range** dialog box, type `0.5` in the **Step** text field.

6 In the **Stop** text field, type `5`.

7 Click **Replace**.

8 In the **Home** toolbar, click **Compute**.

The model should now solve in about a minute or two.

RESULTS

pH (el)

Plots for pH, conductivity, potential, and concentrations are created by default. To compare these to the plots in the Results and Discussion section, proceed as follows for each plot:

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 **Data** section. From the **Time selection** list, choose **From list**.

4 In the **Times (min)** list, choose **0** and **4**.

Line Graph 1

1 In the **Model Builder** window, expand the **pH (el)** node, then click **Line Graph 1**.

2 In the **Settings** window for **Line Graph**, click to expand the **Coloring and Style** section.

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

4 In the **pH (el)** toolbar, click **Plot**.

Molar Concentration - tris (el)

In the **Model Builder** window, expand the **Electrolyte Conductivity (el)** node.

Molar Concentration - HAC (el)

In the **Model Builder** window, expand the **Molar Concentration - tris (el)** node.

Sample Concentrations

You can also create your own plots. Proceed as follows to create a plot that compares the aniline and pyridine concentrations in the same graph.

1 In the **Model Builder** window, expand the **Molar Concentration - HAC (el)** node.

2 Right-click **Molar Concentration - pyr (el)** and choose **Duplicate**.

3 In the **Settings** window for **1D Plot Group**, type `Sample Concentrations` in the **Label** text field.

4 Locate the **Data** section. In the **Times (min)** list, select **1**.

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

Line Graph 1

1 In the **Model Builder** window, expand the **Sample Concentrations** node, then click **Line Graph 1**.

2 In the **Settings** window for **Line Graph**, locate the **y-Axis Data** section.

3 In the **Unit** field, type `mM`.

4 Locate the **x-Axis Data** section. From the **Unit** list, choose **cm**.

5 Locate the **Coloring and Style** section. From the **Width** list, choose **2**.

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

7 In the table, enter the following settings:

Legends
Pyridine

Line Graph 2

1 Right-click **Results>Sample Concentrations>Line Graph 1** and choose **Duplicate**.

2 In the **Settings** window for **Line Graph**, click **Replace Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)> Electrophoretic Transport>Weak Base - ani>el.c_ani - Concentration - mol/m³**.

3 Locate the **Coloring and Style** section. From the **Width** list, choose **2**.

4 Locate the **Legends** section. In the table, enter the following settings:

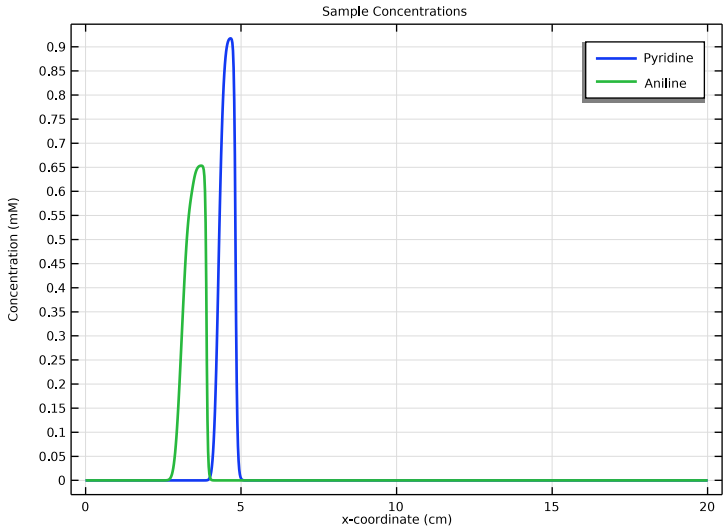
Legends
Aniline

Sample Concentrations

You can now compare the concentrations at 1 and 3 min as follows:

1 In the **Model Builder** window, click **Sample Concentrations**.

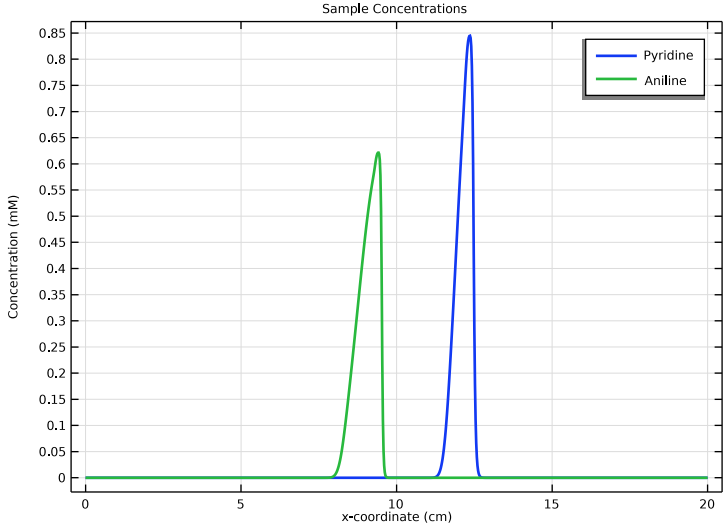
2 In the **Sample Concentrations** toolbar, click **Plot**.



3 In the **Settings** window for **1D Plot Group**, locate the **Data** section.

4 In the **Times (min)** list, select **3**.

5 In the **Sample Concentrations** toolbar, click **Plot**.



Animation 1

You can also create an animation of the plot you just created, for all times stored in the solution.

1. In the **Results** toolbar, click **Animation** and choose **Player**.
2. In the **Settings** window for **Animation**, locate the **Scene** section.
3. From the **Subject** list, choose **Sample Concentrations**.
4. Locate the **Frames** section. From the **Frame selection** list, choose **All**.
5. Locate the **Playing** section. In the **Display each frame for** text field, type `0.5`.
6. Click the **Play** button in the **Graphics** toolbar.

   Increasing the number of frames in the animation can be achieved by decreasing the incremental step of the `range()` operator, for example `range(0,0.1,5)` under **Times** in the **Time Dependent** node, and re-solving.