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Supplementary material

Determination of cupric ion concentrations in marine waters: an improved procedure and comparison with other speciation methods

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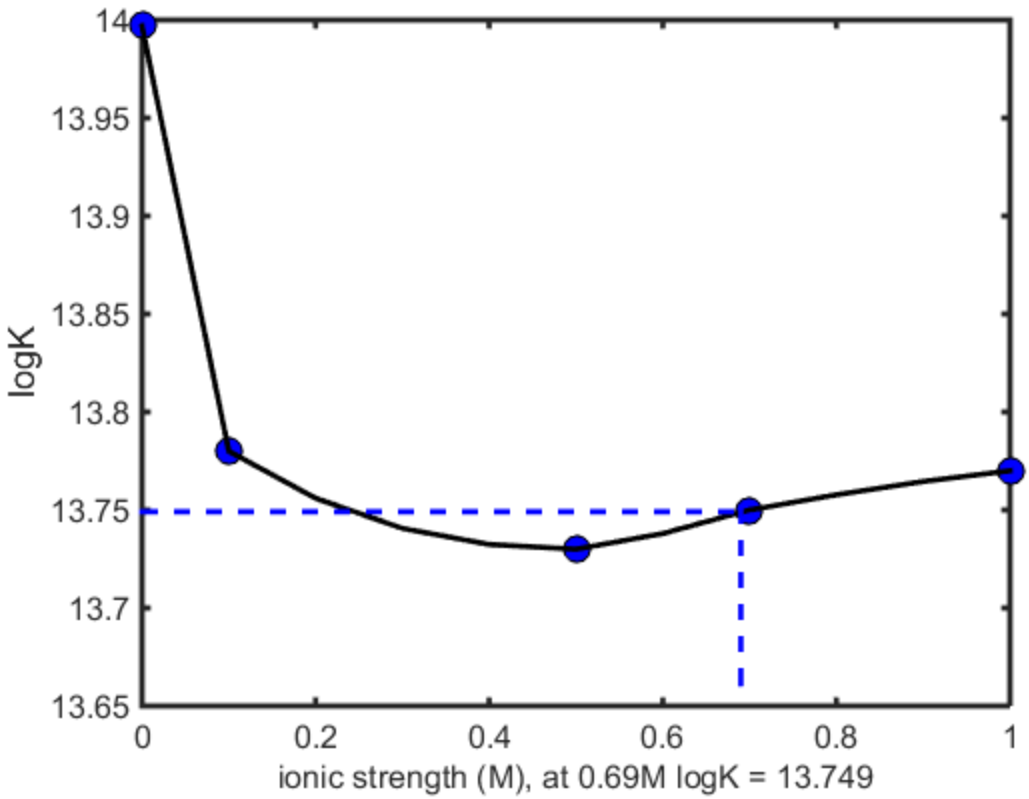
The material below is published from the *Matlab* file used to generate log*K* values for Cu speciation modelling. These log*K* values are based on concentrations not activities. To determine the concentration based log*K* values for seawater ionic strength the tabulated concentration based log*K* values from NIST were interpolated. Seawater ionic strength was calculated as 0.69 M based on the artificial seawater recipe used in this research. Graphs embedded below show the original values from NIST and the interpolated values (represented by dashed lines). In addition, the specific reaction utilised in the tableau for speciation calculations are shown as text associated with each graph.

```
% find seawater appropriate logK values relevant to Cu speciation
% with tryptophan as an added ligand
% just use 25 degrees C values

figure(1); clf
% ionic strength for interpolation

IOpt6=0.69;
```

OH reaction H+OH=H2O

```
I=[0 0.1 0.5 0.7 1];
logK=[13.997 13.78 13.73 13.75 13.77];
Iinterp=0:0.1:1;
YI = interp1(I,logK,Iinterp,'Pchip');

logKcorr = interp1(I,logK,IOpt6,'Pchip'); logKw=-1*logKcorr;
logKcorrtxt=num2str(logKcorr,5);

plot(I,logK,'ko','markersize',10,'markerfacecolor','b')
hold on
plot(Iinterp,YI,'k','linewidth',2)
set(gca,'fontsize',12,'linewidth',2)
isstr=num2str(IOpt6);
txt=['ionic strength (M), at ',isstr,'M logK = ',logKcorrtxt];
xlabel(txt,'fontsize',12)
ylabel('logK')
plot([IOpt6 IOpt6],[min(logK)-0.005*(min(logK)) logKcorr],'b--','linewidth',2)
plot([0 IOpt6],[logKcorr logKcorr],'b--','linewidth',2)

logKw=logKw
```

```
logKw =

  -13.7491
```

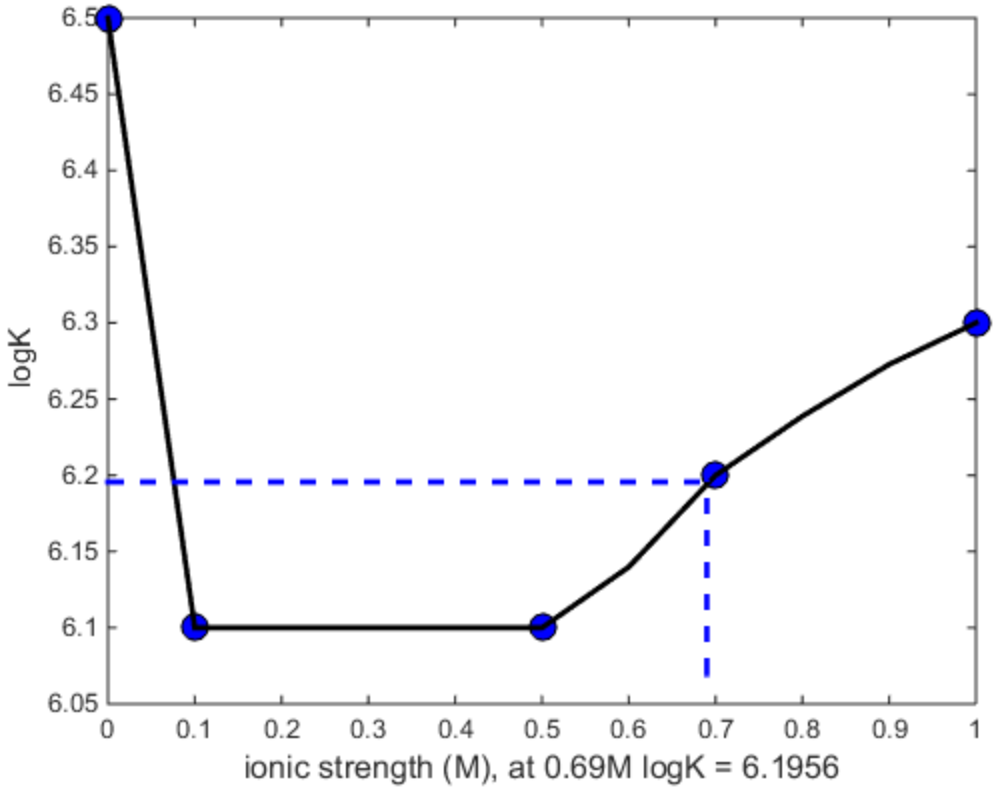




```
% CuOH
% reaction Cu+OH=CuOH
```

```
figure(1); clf

I=[0 0.1 0.5 0.7 1];
logK=[6.5 6.1 6.1 6.2 6.3];
Iinterp=0:0.1:1;
YI = interp1(I,logK,Iinterp,'Pchip');


logKcorr = interp1(I,logK,IOpt6,'Pchip'); logKOH1=logKcorr;
logKcorrtxt=num2str(logKcorr,5);

plot(I,logK,'ko','markersize',10,'markerfacecolor','b')
hold on
plot(Iinterp,YI,'k','linewidth',2)
isstr=num2str(IOpt6);
txt=['ionic strength (M), at ',isstr,'M logK = ',logKcorrtxt];
xlabel(txt,'fontsize',12)
ylabel('logK')
plot([IOpt6 IOpt6],[min(logK)-0.005*(min(logK)) logKcorr],'b--','linewidth',2)
plot([0 IOpt6],[logKcorr logKcorr],'b--','linewidth',2)
```

```
%Cu+H2O=CuOH for tableau
logKh1=logKOH1+logKw
```

```
logKh1 =

   -7.5535
```



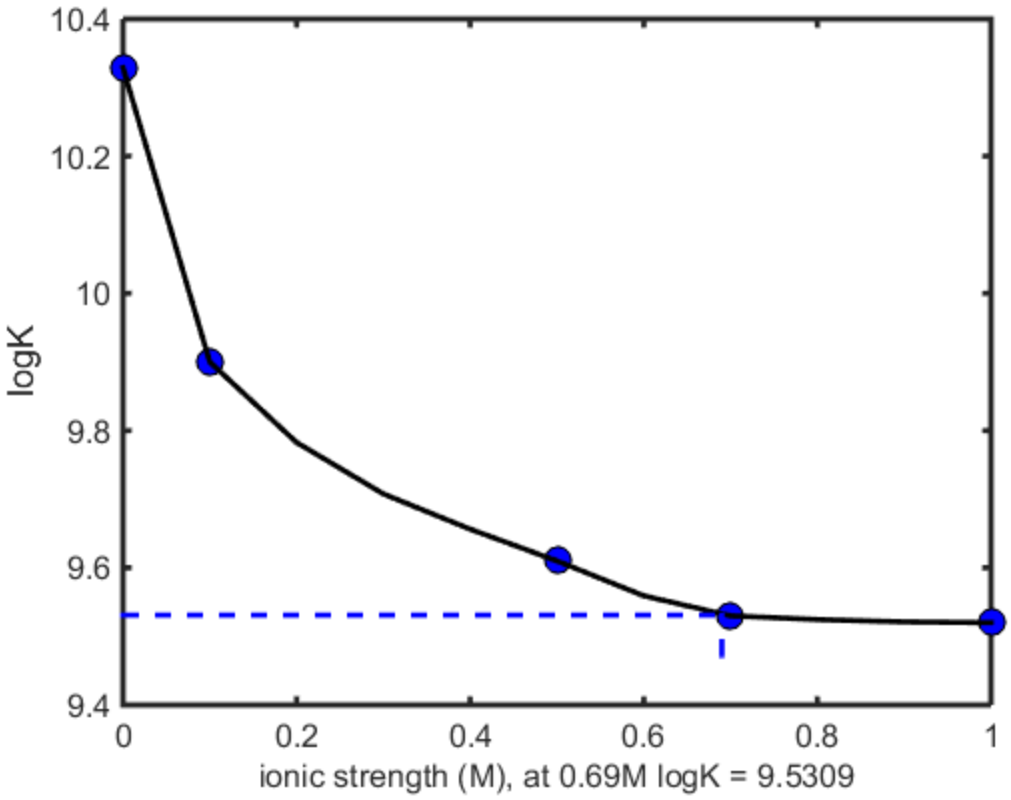

```
% H2CO3
% reaction CO3+H=HCO3
```

```
figure(1); clf

I=[0 0.1 0.5 0.7 1.0];
logK=[10.329 9.90 9.61 9.53 9.52];
Iinterp=0:0.1:1;
YI = interp1(I,logK,Iinterp,'Pchip');


logKcorr = interp1(I,logK,IOpt6,'Pchip'); logKa2=logKcorr;
logKcorrtxt=num2str(logKcorr,5);

plot(I,logK,'ko','markersize',10,'markerfacecolor','b')
hold on
```



```
plot(Iinterp,YI,'k','linewidth',2)
set(gca,'fontsize',12,'linewidth',2)
isstr=num2str(IOpt6);
txt=['ionic strength (M), at ',isstr,'M logK = ',logKcorrtxt];
xlabel(txt,'fontsize',12)
ylabel('logK')
plot([IOpt6 IOpt6],[min(logK)-0.005*(min(logK)) logKcorr],'b--','linewidth',2)
plot([0 IOpt6],[logKcorr logKcorr],'b--','linewidth',2)
%H+CO3=HCO3 for tableau
logKa2=logKa2

print H2CO3pKa2.eps -depsc2
```

```
logKa2 =

    9.5309
```

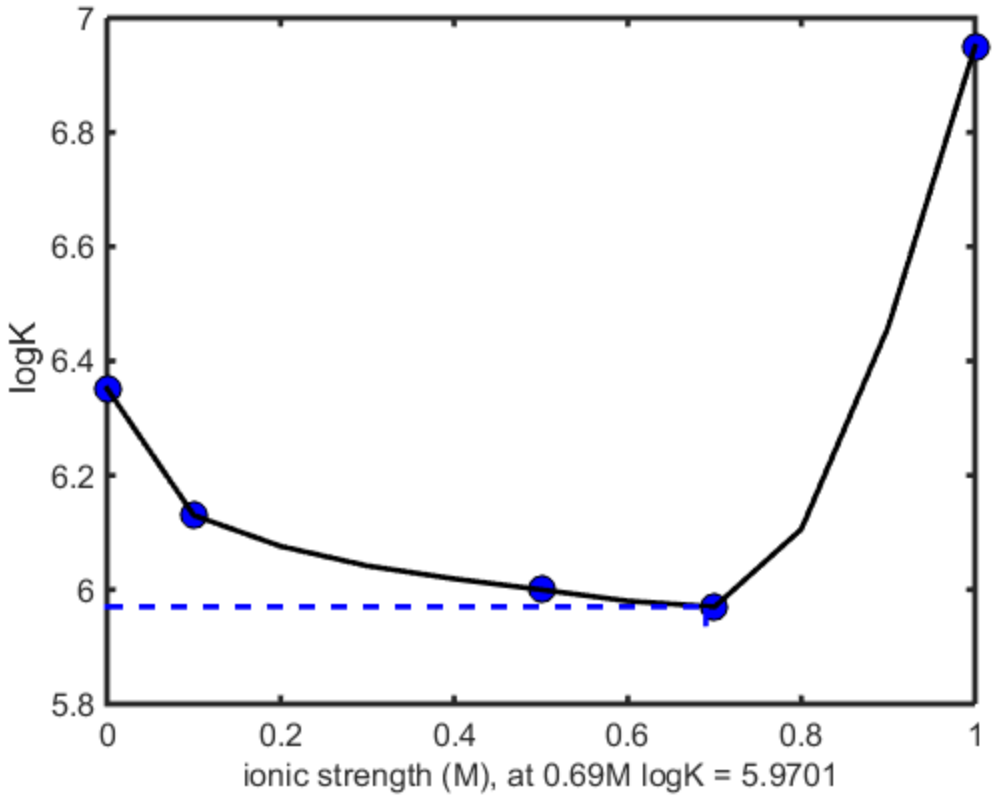



```
% H2CO3
% reaction HCO3+H=H2CO3
figure(1); clf

I=[0 0.1 0.5 0.7 1.0];
```



```
logK=[6.352 6.13 6.00 5.97 6.95];
Iinterp=0:0.1:1;
YI = interp1(I,logK,Iinterp,'Pchip');


logKcorr = interp1(I,logK,IOpt6,'Pchip'); logBa2=logKcorr+logKa2;
logKcorrtxt=num2str(logKcorr,5);

plot(I,logK,'ko','markersize',10,'markerfacecolor','b')
hold on
plot(Iinterp,YI,'k','linewidth',2)
set(gca,'fontsize',12,'linewidth',2)
isstr=num2str(IOpt6);
txt=['ionic strength (M), at ',isstr,'M logK = ',logKcorrtxt];
xlabel(txt,'fontsize',12)
ylabel('logK')
plot([IOpt6 IOpt6],[min(logK)-0.005*(min(logK)) logKcorr],'b--','linewidth',2)
plot([0 IOpt6],[logKcorr logKcorr],'b--','linewidth',2)

print H2CO3pKa1.eps -depsc2

%2H+CO3=H2CO3 for tableau
logBa2=logBa2
```

```
logBa2 =

   15.5011
```

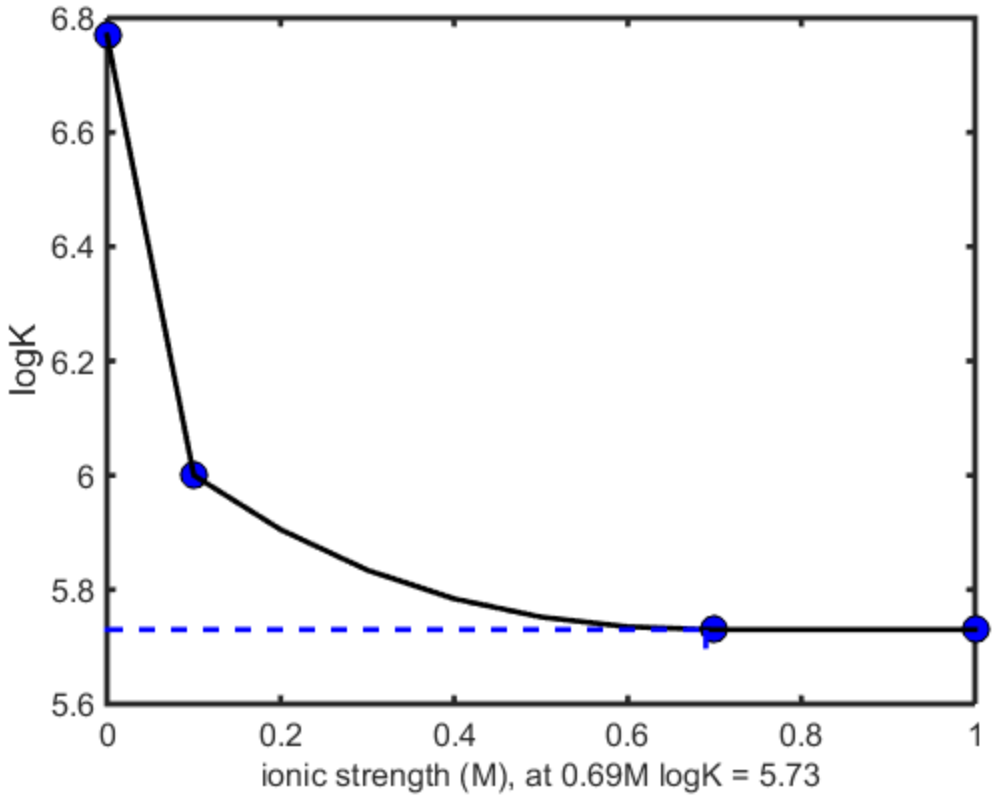



H2CO3 reaction Cu+CO3=CuCO3

```
figure(1); clf

I=[0 0.1 0.7 1];
logK=[6.77 6 5.73 5.73];
Iinterp=0:0.1:1;
YI = interp1(I,logK,Iinterp,'Pchip');


logKcorr = interp1(I,logK,IOpt6,'Pchip'); logKCuCO3=logKcorr;
logKcorrtxt=num2str(logKcorr,5);

plot(I,logK,'ko','markersize',10,'markerfacecolor','b')
hold on
plot(Iinterp,YI,'k','linewidth',2)
set(gca,'fontsize',12,'linewidth',2)
isstr=num2str(IOpt6);
txt=['ionic strength (M), at ',isstr,'M logK = ',logKcorrtxt];
xlabel(txt,'fontsize',12)
ylabel('logK')
plot([IOpt6 IOpt6],[min(logK)-0.005*(min(logK)) logKcorr],'b--','linewidth',2)
plot([0 IOpt6],[logKcorr logKcorr],'b--','linewidth',2)
```

```
%Cu+CO3=CuCO3 for tableau
logKCuCO3=logKCuCO3
```

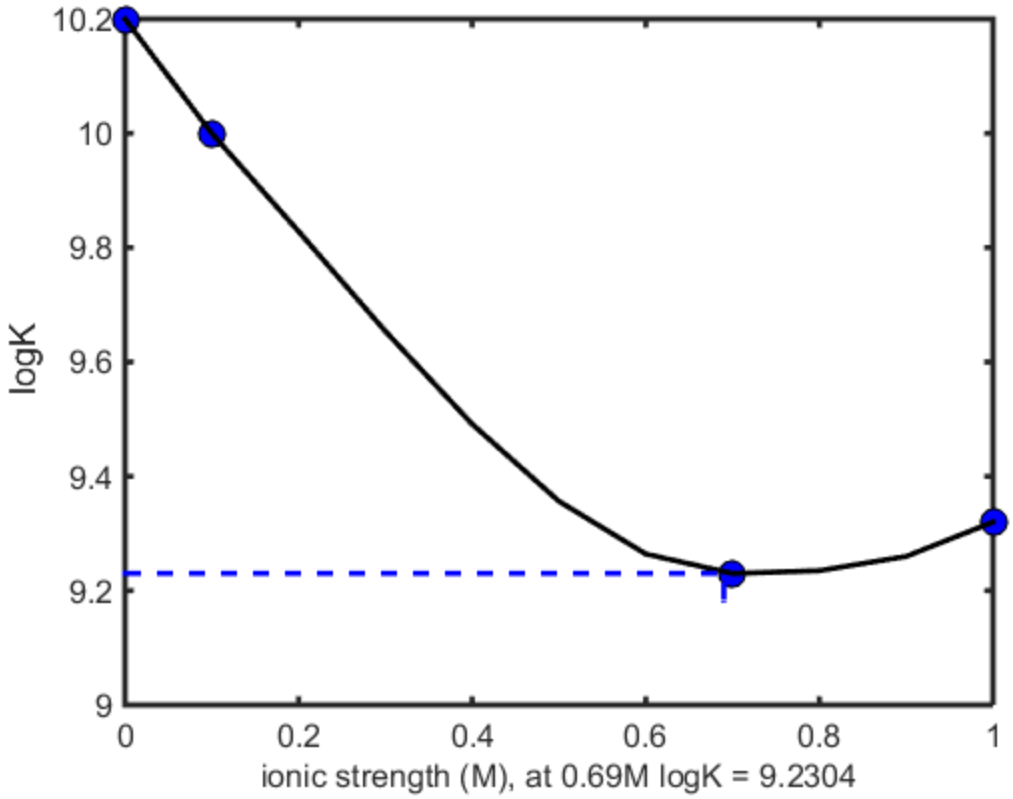
```
logKCuCO3 =

    5.7300
```




```
% H2CO3
% reaction Cu+2CO3=Cu(CO3)2
figure(1); clf

I=[0 0.1 0.7 1];
logK=[10.2 10 9.23 9.32];
Iinterp=0:0.1:1;
YI = interp1(I,logK,Iinterp,'Pchip');


logKcorr = interp1(I,logK,IOpt6,'Pchip'); logKCuCO32=logKcorr;
logKcorrtxt=num2str(logKcorr,5);

plot(I,logK,'ko','markersize',10,'markerfacecolor','b')
hold on
```

```
plot(Iinterp,YI,'k','linewidth',2)
set(gca,'fontsize',12,'linewidth',2)
isstr=num2str(IOpt6);
txt=['ionic strength (M), at ',isstr,'M logK = ',logKcorrtxt];
xlabel(txt,'fontsize',12)
ylabel('logK')
plot([IOpt6 IOpt6],[min(logK)-0.005*(min(logK)) logKcorr],'b--','linewidth',2)
plot([0 IOpt6],[logKcorr logKcorr],'b--','linewidth',2)
%Cu+2CO3=Cu(CO3)2 for tableau
logKCuCO32=logKCuCO32
```

```
logKCuCO32 =

    9.2304
```

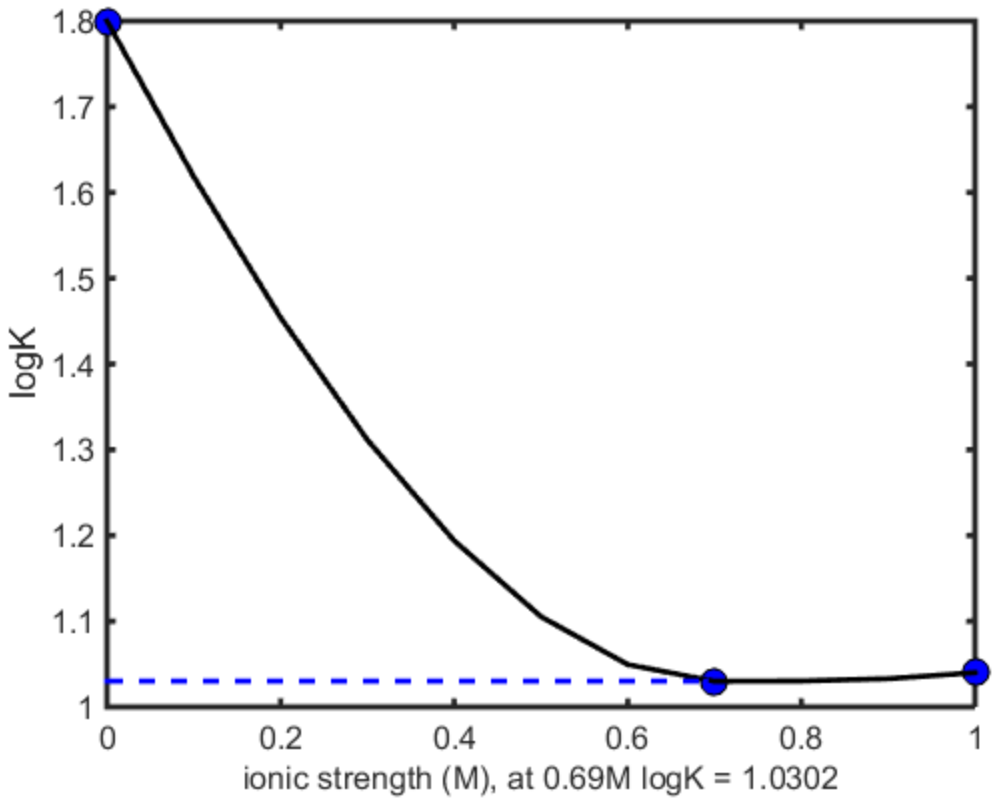



```
% H2CO3
% reaction Cu+HCO3=CuHCO3
```

```
figure(1); clf

I=[0 0.7 1];
logK=[1.8 1.03 1.04];
Iinterp=0:0.1:1;
```

```
YI = interp1(I,logK,Iinterp,'Pchip');


logKcorr = interp1(I,logK,IOpt6,'Pchip'); logKCuHCO3=logKcorr;
logKcorrtxt=num2str(logKcorr,5);

plot(I,logK,'ko','markersize',10,'markerfacecolor','b')
hold on
plot(Iinterp,YI,'k','linewidth',2)
set(gca,'fontsize',12,'linewidth',2)
isstr=num2str(IOpt6);
txt=['ionic strength (M), at ',isstr,'M logK = ',logKcorrtxt];
xlabel(txt,'fontsize',12)
ylabel('logK')
plot([IOpt6 IOpt6],[min(logK)-0.005*(min(logK)) logKcorr],'b--','linewidth',2)
plot([0 IOpt6],[logKcorr logKcorr],'b--','linewidth',2)
%Cu+CO3+H=CuHCO3 for tableau
logKCuHCO3=logKCuHCO3+logKa2
```

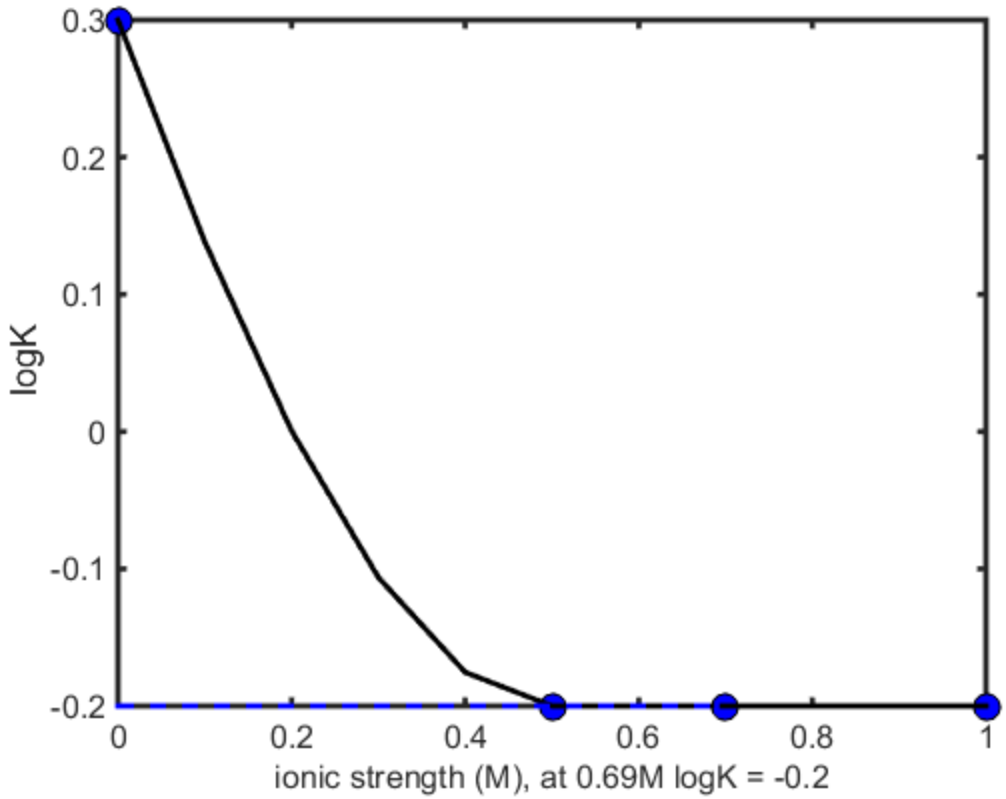
```
logKCuHCO3 =

   10.5611
```




```
% CuCl
% reaction Cu+Cl=CuCl
```

```
figure(1); clf

I=[0 0.5 0.7 1.0];
logK=[0.3 -0.2 -0.2 -0.2];
Iinterp=0:0.1:1;
YI = interp1(I,logK,Iinterp,'Pchip');


logKcorr = interp1(I,logK,IOpt6,'Pchip'); logKCuCl=logKcorr;
logKcorrtxt=num2str(logKcorr,5);

plot(I,logK,'ko','markersize',10,'markerfacecolor','b')
hold on
plot(Iinterp,YI,'k','linewidth',2)
set(gca,'fontsize',12,'linewidth',2)
isstr=num2str(IOpt6);
txt=['ionic strength (M), at ',isstr,'M logK = ',logKcorrtxt];
xlabel(txt,'fontsize',12)
ylabel('logK')
plot([IOpt6 IOpt6],[min(logK)-0.005*(min(logK)) logKcorr],'b--','linewidth',2)
plot([0 IOpt6],[logKcorr logKcorr],'b--','linewidth',2)
%Cu+Cl=CuCl for tableau
logKCuCl=logKCuCl
```

```
logKCuCl =

   -0.2000
```

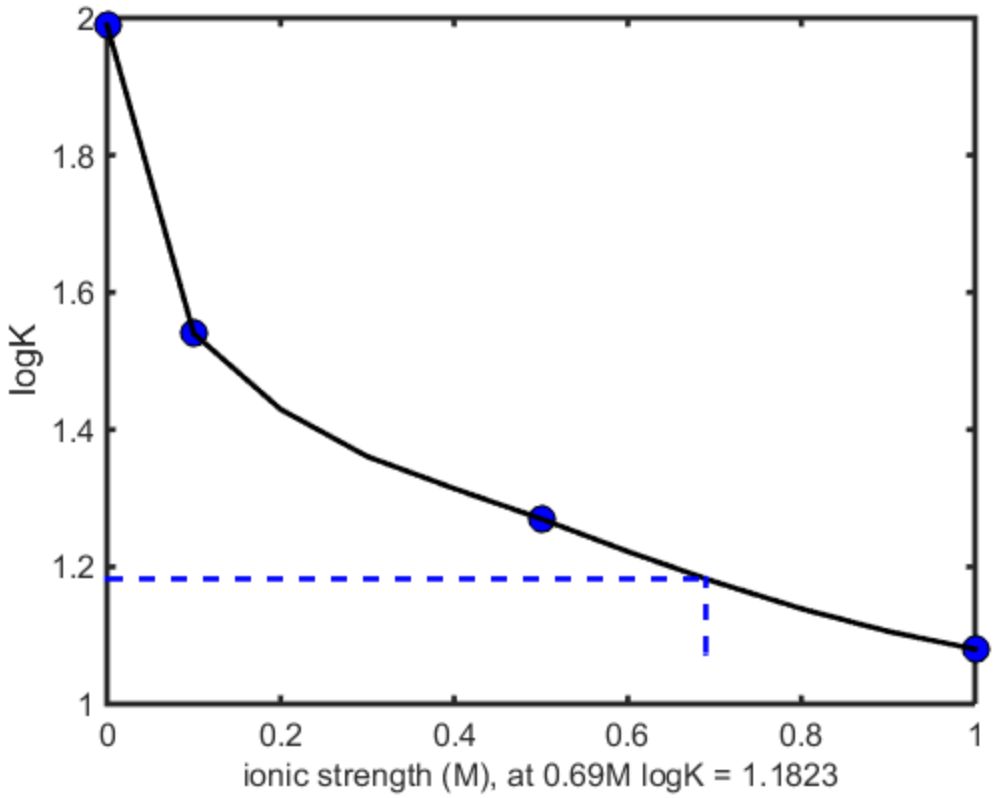




```
% SO4
% reaction SO4+H=HSO4
```

```
figure(1); clf

I=[0 0.1 0.5 1];
logK=[1.99 1.54 1.27 1.08];
Iinterp=0:0.1:1;
YI = interp1(I,logK,Iinterp,'Pchip');


logKcorr = interp1(I,logK,IOpt6,'Pchip'); logKHSO4=logKcorr;
logKcorrtxt=num2str(logKcorr,5);

plot(I,logK,'ko','markersize',10,'markerfacecolor','b')
hold on
plot(Iinterp,YI,'k','linewidth',2)
set(gca,'fontsize',12,'linewidth',2)
isstr=num2str(IOpt6);
txt=['ionic strength (M), at ',isstr,'M logK = ',logKcorrtxt];
xlabel(txt,'fontsize',12)
ylabel('logK')
plot([IOpt6 IOpt6],[min(logK)-0.005*(min(logK)) logKcorr],'b--','linewidth',2)
plot([0 IOpt6],[logKcorr logKcorr],'b--','linewidth',2)
```

```
%H+SO4=HSO4 for tableau
logKHSO4=logKHSO4
```

```
logKHSO4 =

    1.1823
```



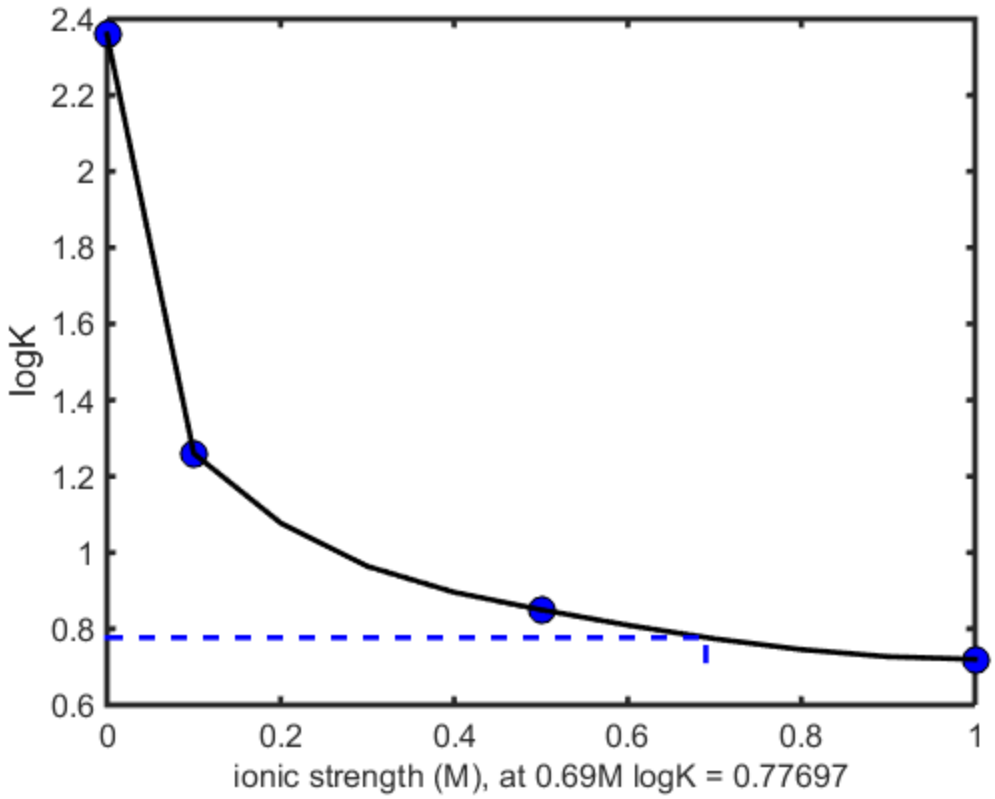

```
% SO4
% reaction SO4+Cu=CuSO4
```

```
figure(1); clf

I=[0 0.1 0.5 1];
logK=[2.36 1.26 0.85 0.72];
Iinterp=0:0.1:1;
YI = interp1(I,logK,Iinterp,'Pchip');


logKcorr = interp1(I,logK,IOpt6,'Pchip'); logKCuSO4=logKcorr;
logKcorrtxt=num2str(logKcorr,5);

plot(I,logK,'ko','markersize',10,'markerfacecolor','b')
hold on
```



```
plot(Iinterp,YI,'k','linewidth',2)
set(gca,'fontsize',12,'linewidth',2)
isstr=num2str(IOpt6);
txt=['ionic strength (M), at ',isstr,'M logK = ',logKcorrtxt];
xlabel(txt,'fontsize',12)
ylabel('logK')
plot([IOpt6 IOpt6],[min(logK)-0.005*(min(logK)) logKcorr],'b--','linewidth',2)
plot([0 IOpt6],[logKcorr logKcorr],'b--','linewidth',2)

%Cu+SO4=CuSO4 for tableau
logKCuSO4=logKCuSO4
```

```
logKCuSO4 =

    0.7770
```

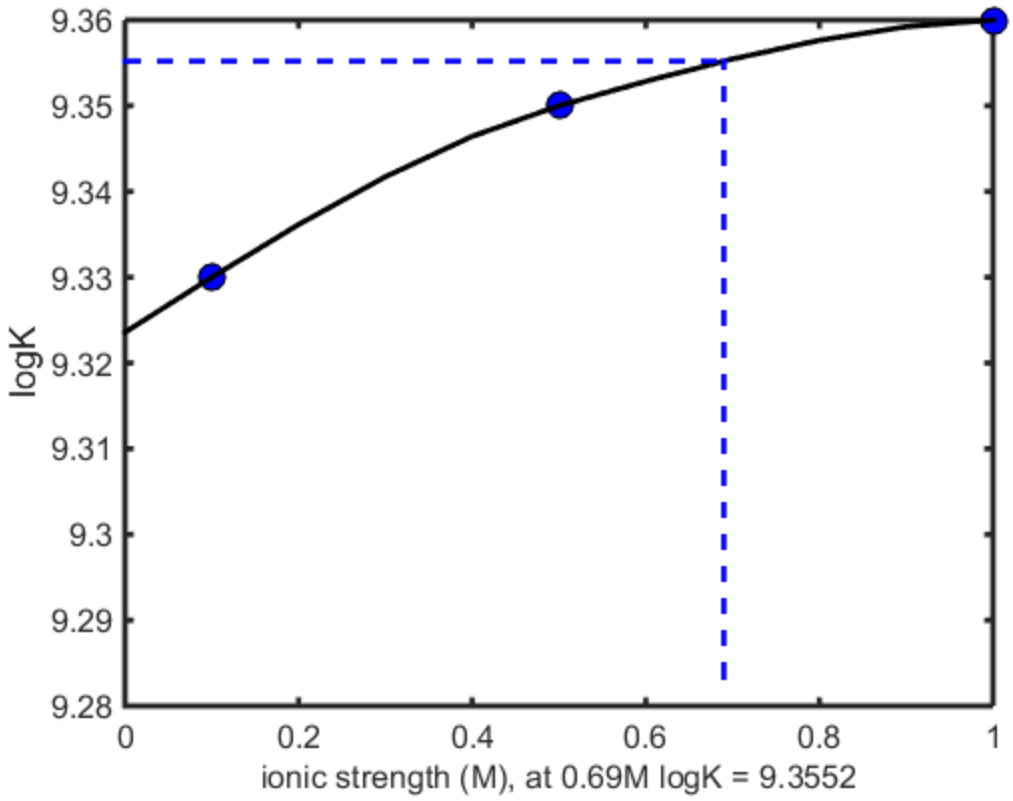



```
% Trp
% reaction H+Trp=HTrp

figure(1); clf

I=[0.1 0.5 1.0];
logK=[9.33 9.35 9.36];
```



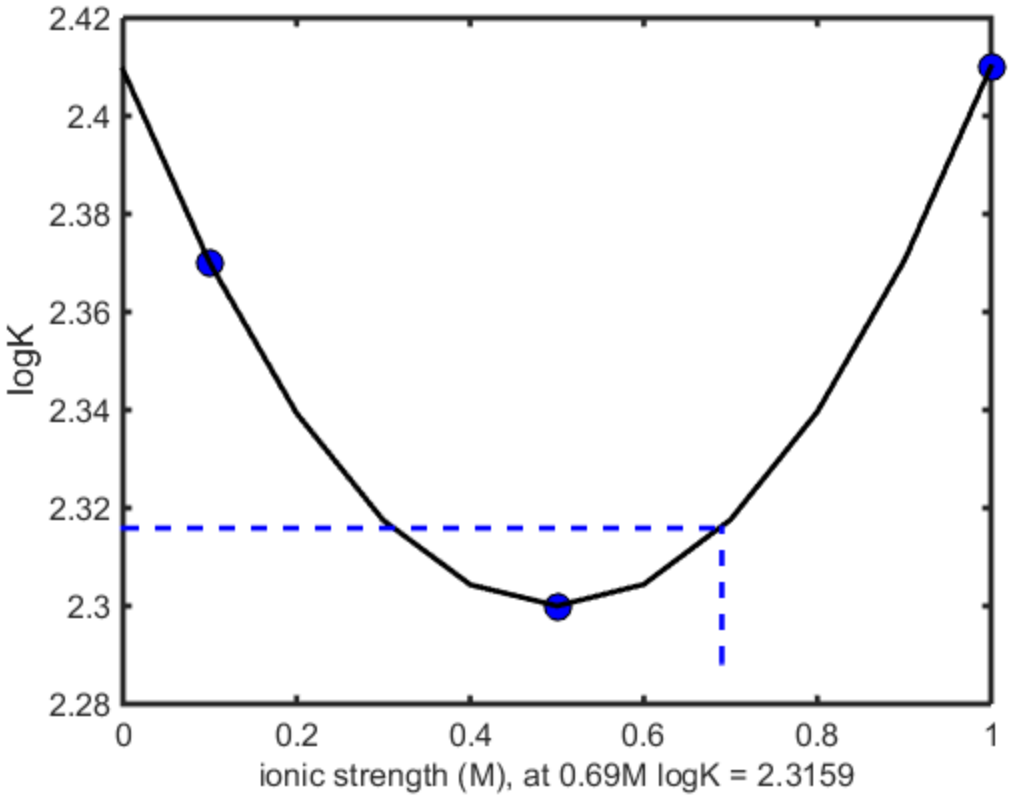
```
Iinterp=0:0.1:1;
YI = interp1(I,logK,Iinterp,'Pchip');


logKcorr = interp1(I,logK,IOpt6,'Pchip'); logKHTrp=logKcorr;
logKcorrtxt=num2str(logKcorr,5);

plot(I,logK,'ko','markersize',10,'markerfacecolor','b')
hold on
plot(Iinterp,YI,'k','linewidth',2)
set(gca,'fontsize',12,'linewidth',2)
isstr=num2str(IOpt6);
txt=['ionic strength (M), at ',isstr,'M logK = ',logKcorrtxt];
xlabel(txt,'fontsize',12)
ylabel('logK')
plot([IOpt6 IOpt6],[min(logK)-0.005*(min(logK)) logKcorr],'b--','linewidth',2)
plot([0 IOpt6],[logKcorr logKcorr],'b--','linewidth',2)

%H+Trp=HTrp for tableau
logKHTrp=logKHTrp
```

```
logKHTrp =

    9.3552
```




```
% Trp
% reaction H+HTrp=H2Trp

figure(1); clf

I=[0.1 0.5 1.0];
logK=[2.37 2.30 2.41];
Iinterp=0:0.1:1;
YI = interp1(I,logK,Iinterp,'Pchip');


logKcorr = interp1(I,logK,IOpt6,'Pchip'); logKH2Trp=logKcorr;
logKcorrtxt=num2str(logKcorr,5);

plot(I,logK,'ko','markersize',10,'markerfacecolor','b')
hold on
plot(Iinterp,YI,'k','linewidth',2)
set(gca,'fontsize',12,'linewidth',2)
isstr=num2str(IOpt6);
txt=['ionic strength (M), at ',isstr,'M logK = ',logKcorrtxt];
xlabel(txt,'fontsize',12)
ylabel('logK')
plot([IOpt6 IOpt6],[min(logK)-0.005*(min(logK)) logKcorr],'b--','linewidth',2)
plot([0 IOpt6],[logKcorr logKcorr],'b--','linewidth',2)

%2H+Trp=H2Trp for tableau
logKH2Trp=logKH2Trp+logKHTrp
```

```
logKH2Trp =

   11.6711
```

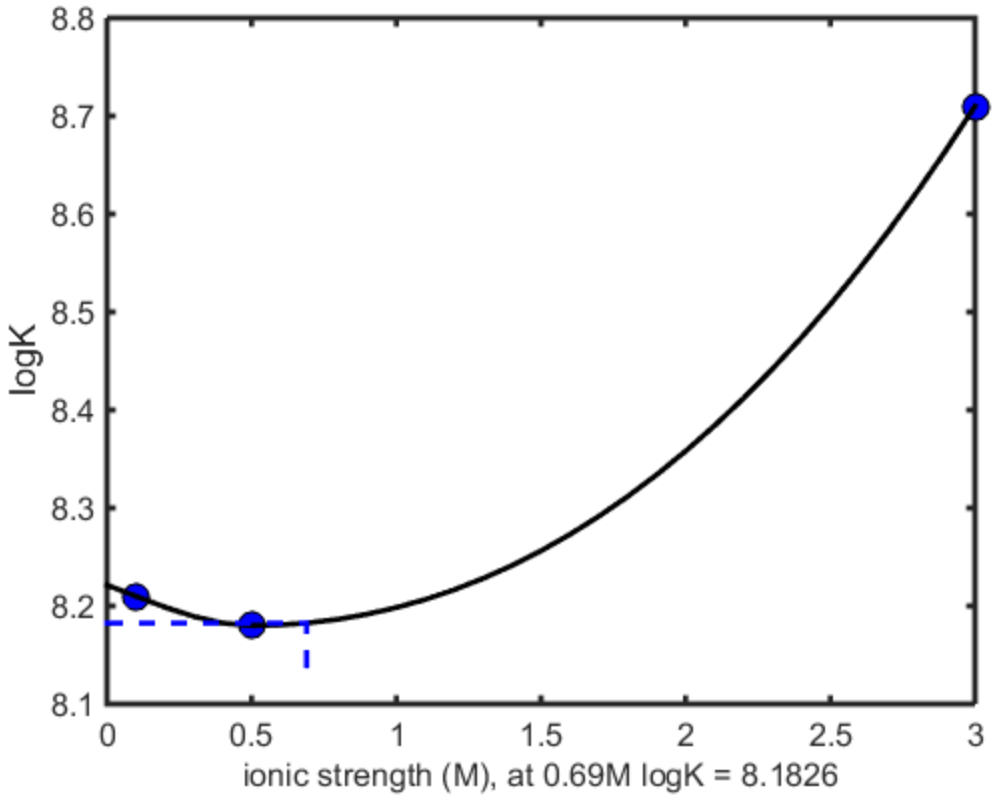

```
% Trp
% reaction Cu+Trp=CuTrp
```

```
figure(1); clf

I=[0.1 0.5 3.0];
logK=[8.21 8.18 8.71];
Iinterp=0:0.1:3;
YI = interp1(I,logK,Iinterp,'Pchip');


logKcorr = interp1(I,logK,IOpt6,'Pchip'); logKCuTrp=logKcorr;
logKcorrtxt=num2str(logKcorr,5);

plot(I,logK,'ko','markersize',10,'markerfacecolor','b')
hold on
plot(Iinterp,YI,'k','linewidth',2)
set(gca,'fontsize',12,'linewidth',2)
isstr=num2str(IOpt6);
txt=['ionic strength (M), at ',isstr,'M logK = ',logKcorrtxt];
xlabel(txt,'fontsize',12)
ylabel('logK')
plot([IOpt6 IOpt6],[min(logK)-0.005*(min(logK)) logKcorr],'b--','linewidth',2)
plot([0 IOpt6],[logKcorr logKcorr],'b--','linewidth',2)
```



```
%Cu+Trp=CuTrp for tableau
logKCuTrp=logKCuTrp
```

```
logKCuTrp =

    8.1826
```

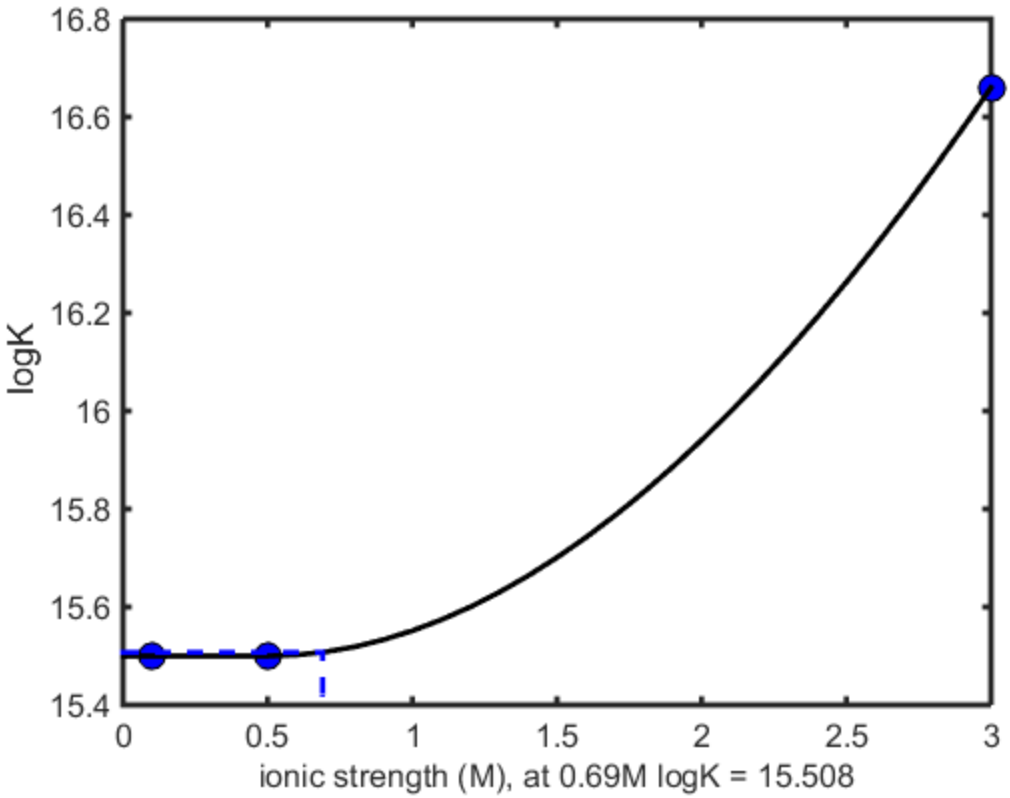



```
% Trp
% reaction Cu+Trp2=CuTrp2
figure(1); clf

I=[0.1 0.5 3.0];
logK=[15.5 15.5 16.66];
Iinterp=0:0.1:3;
YI = interp1(I,logK,Iinterp,'Pchip');


logKcorr = interp1(I,logK,IOpt6,'Pchip'); logKCuTrp2=logKcorr;
logKcorrtxt=num2str(logKcorr,5);

plot(I,logK,'ko','markersize',10,'markerfacecolor','b')
hold on
```



```
plot(Iinterp,YI,'k','linewidth',2)
set(gca,'fontsize',12,'linewidth',2)
isstr=num2str(IOpt6);
txt=['ionic strength (M), at ',isstr,'M logK = ',logKcorrtxt];
xlabel(txt,'fontsize',12)
ylabel('logK')
plot([IOpt6 IOpt6],[min(logK)-0.005*(min(logK)) logKcorr],'b--','linewidth',2)
plot([0 IOpt6],[logKcorr logKcorr],'b--','linewidth',2)

%Cu+Trp=CuTrp for tableau
logKCuTrp2=logKCuTrp2
```

```
logKCuTrp2 =

   15.5076
```



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