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Supporting information

A Mathematical Model for Kinetic Study of Analyte Permeation Both from Liquid and Gas Phase through Hollow Fiber Membranes into Vacuum

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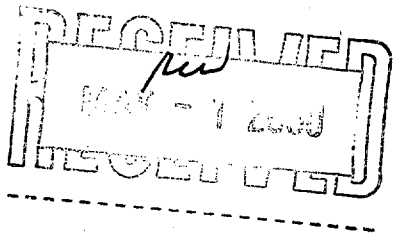

Texts of Matlab script files:

1. Mem_ns_demo.m	Matlab5 script file for simulation of nonsteady state permeation of a compound through a capillary membrane into vacuum.
2. Mob_st_demo.m	Matlab5 script file for calculation of steady state analyte concentration distribution in liquid mobile phase pumped through a lumen of a capillary membrane while other side of the membrane is exposed to vacuum.
3. Mob_ns_demo.m	Matlab5 script file for simulation of analyte concentration redistribution in liquid mobile phase pumped through a lumen of a capillary membrane while other side of the membrane is exposed to vacuum.

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Mem_ns_demo.m

```
script

% This is a Matlab5 script file for simulation of NON-STEADY-STATE PERMEATION
% of a compound through a capillary membrane into vacuum.

% At every time step this script file calculates concentration profiles in the
% membrane (one-dimensional problem C=C(r,t)) and permeating flux into vacuum.
% Parameters of experiment, initial concentration profile in the membrane and time
% dependence of analyte concentration in contacting layer of mobile phase
% are used as initial conditions.

% For PERMEATION FROM GAS PHASE, analyte concentration in contacting layer of
% mobile phase at every time step is the same as analyte concentration in
% mobile phase in this time step. That is why in this case time dependence of
% analyte concentration in mobile phase is used as initial condition.

% For PERMEATION FROM LIQUID PHASE, analyte concentration in contacting layer of
% mobile phase at every time step first should be calculated using mob_ns_demo.m
% Matlab5 script file. Afterwards this data should be downloaded into this program.
% Because recommended time step for monitoring depleted layer formation
% (0.005-0.01 seconds) much smaller than recommended time of membrane permeation
% (0.5-1 seconds), it is better to make time-concentration array more sparse.
% Note, that the code mob_ns_demo.m requires significant time resources for execution.
% That is why I recommend using steady-state mobile phase concentration
% distribution (obtainable by mob_st_demo.m) and using mob_ns_demo.m only for
% informative time intervals those corresponds to the processes of concentration
% redistribution in mobile phase.

% Written by Alexey A. Sysoev (alexey.sysoev@msl.mephi.ru) 8 Dec 1998
% Modified 18 Mar 2000

clear all
tic

% Defining parameters of the experiment
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
NN=101; % Number of thickness (r) points
P=121; % Number of time points
Nav=6.022*10^23; % Avogadro constant
lcap=2.5; % length of capillary [cm]
a=0.0305/2; % Inner radius [cm]
b=0.0635/2; % Outer radius [cm]
tall=120; % time of experiment [s]

D=4.9*10^-6; % Diffusivity of the compound in the membrane material [cm^2/s]
K=576;       % Phase distribution coefficient [(mole/cm^3)/(mole/cm^3)]
Vg=22.4e3;   % Gas molar volume [cm^3/mole]

% Setting time dependence of concentration in mobile phase [mole/mole]
% Array Cm(1:P) corresponds to relative concentration in contact zone of
% mobile phase in every time step

% For mobile gas phase Cm(1:P) corresponds to analyte concentration in mobile phase
% at every time step (scenario of analysis)
Cmrel=1*10^-6; %Relative sample concentration [mole/mole]
Cm(1)=0;
Cm(2:(P-1)*2/3)=Cmrel/Vg;
Cm((P-1)*2/3+1:P)=0;
```

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```
% For mobile liquid phase array Cm(1:P) first should be calculated.
% Array Cm(1:P) can be dounloaded from file Cmtime.mat by following line
% load Cmtime; % Dimension of Cmtime should be equal to P (number of time points)
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Setting new variables
Tall=D*tall;
dT=Tall/(P-1);
dX=log(b/a)/(NN-1);

i=1:NN;
X=log(a/b)+(i-1)*dX;
r=b*exp(X);

k=1:P;
T=dT*(k-1);
t=T/D;

% Setting initial data condition
% Calculation of time dependance of concentration in inner diameter of a membrane
Ca=Cm*K;

% Setting initial concentration inside membrane
C0=Ca(1)*X/log(a/b);
C0=C0(:);

% Setting net function
f=dT/(2*dX^2*b^2)*exp(-2*X);
f=f(:);

B=sparse(NN,1);
Ctime=zeros(P,NN);

for k=1:P
   % Setting matrix A and array B
   B(1)=Ca(k);
   B(2:NN-1)=f(2:NN-1).*C0(1:NN-2)+(1-2*f(2:NN-1)).*C0(2:NN-1)+f(2:NN-1).*C0(3:NN);

   D0=ones(NN,1);
   D0(2:NN-1)=1+2*f(2:NN-1);

   D1=zeros(NN,1);
   D1(3:NN)=-f(2:NN-1);

   Dm1=zeros(NN,1);
   Dm1(1:NN-2)=-f(2:NN-1);

   DD=[Dm1 D0 D1];
   clear Dm1 D0 D1
   ddd=[-1 0 1];
   A=spdiags(DD,ddd,NN,NN);

   % Solving system of equations
   C=A\B;
   % Defining time-concentration matrix
   Ctime(k,:)=C';
   % Determining initial condition for the next step
   C0=C;
end

f=D*exp(-X(NN-1))/(2*b*dX)*(Ctime(:,NN-2)-Ctime(:,NN));
```

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```
% f - permeating flux into vacuum at different time steps
% Ctime - concentration profiles in membrane phase at different time intervals,
mol/cm^3
toc

% Results
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
hold on

% Plotting concentration profiles in membrane phase at different time intervals
figure(1)
for k=2:7:(P-1)/2
   plot(r,Ctime(k,:))
end
xlabel('Radius, cm')
ylabel('Concentration, mol/cm^3')
title('Concentration profiles in membrane phase')
grid on
zoom on
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%Ftest=2*pi*D*lcap*Ca(2)*Nav/log(b/a) %Steady state permeating flux

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Plotting permeating flux dynamics
figure(2)
F=f*lcap*2*pi*r(NN-1)*Nav;
F=F/max(F);

plot(t,F)
xlabel('time, sec')
ylabel('flow, relative units')
title('Permeating flux dynamics')
grid on
zoom on
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
```

Mob_st_demo.m

```
script

% This is a Matlab5 script file for calculation of steady-state analyte
% concentration distribution in liquid mobile phase pumped through a lumen of a
% capillary membrane while other side of the membrane is exposed to vacuum.

% This script file calculates concentration profile in mobile phase
% (two-dimensional problem C=C(r,z)) and permeating flux. Parameters of the
% experiment initial concentration profile in mobile phase and time dependence
% of analyte concentration in inlet cross-section of mobile phase (scenario of
% analysis) are used as initial conditions.

% Written by Alexey A. Sysoev (alexey.sysoev@msl.mephi.ru) 18 Dec 1998
% Modified 18 Mar 2000

clear all
tic

% Defining parameters of the experiment
```

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
N=101; % Number of thickness (r) points
M=101; % Number of length (L) points
Nav=6.022*10^23; % Avogadro constant
lcap=2.5;        % length of capillary 2.5 [cm]
a=0.0305/2;      % Inner radius [cm]
b=0.0635/2;      % Outer radius [cm]
Pt=75.8;         % Atmosphere pressure [cmHg]
Cmrel=1*10^-6;   % Relative concentration
Vm=18;           % Water molar volume [cm^3/mol]

V0=2*0.0167;  % Rate of pumping [cm^3/sec], 1 ml/min = 0.0167 cm^3/sec

D=4.9*10^-6;  % Diffusivity in membrane [cm^2/s]
Dm=7.5*10^-6; % Diffusivity in mobile phase [cm^2/s]
K=171.8;      % Phase distribution coefficient [(mole/cm^3)/(mole/cm^3)
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

Cmv=Cmrel/Vm; %Molar volume concentration [mol/cm^3]
dr=a/(N-1);
dz=lcap/(M-1);

pp=D/Dm*K/(a*log(b/a));

D0=zeros(N,M);
D0(1:N,1)=ones(N,1);
D0(1:N,M)=ones (N,1);
D0(1,2:M-1)=ones(1,M-2);
D0(N,2:M-1)=ones(1,M-2)+dr*pp;
r=[0:dr:a];
r=r(:);
r(N)=[];
r(1)=[];
D0(2:N-1,2:M-1)=repmat(-2*r/dr^2,1,M-2);
D0=D0(:);

D1=zeros(N,M);
D1(1,2:M-1)=-ones(1,M-2);
D1(2:N-1,2:M-1)=repmat(r/dr^2+1/(2*dr),1,M-2);
D1=D1(:);
D1=[0;D1];
D1(M*N+1,:)=[];

Dm1=zeros(N,M);
Dm1(N,2:M-1)=-ones(1,M-2);
Dm1(2:N-1,2:M-1)=repmat(r/dr^2-1/(2*dr),1,M-2);
Dm1=Dm1(:);
Dm1(1,:)=[];
Dm1=[Dm1;0];

DN=zeros(N,M);
f=2*V0/(Dm*pi*a^2)*r.*(1-r.*r/a^2);
clear r
DN(2:N-1,2:M-1)=repmat(-f/(2*dz),1,M-2);
DN=DN(:);
DN=[zeros(N,1);DN];
DN(N*M+1:N*M+N,:)=[];

DmN=zeros(N,M);
DmN(1:N,M)=-ones(N,1);
DmN(2:N-1,2:M-1)=repmat(f/(2*dz),1,M-2);
```

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```
clear f
DmN=DmN(:);
DmN(1:N,:)=[];
DmN=[DmN;zeros(N,1)];

%Dm2=sparse(N,M);
%Dm2(N,2:M-1)=1;
%Dm2=Dm2(:);
%Dm2(1:2,:)=[];
%Dm2=[Dm2;0;0];

DD=[DmN Dm1 D0 D1 DN];
clear DmN Dm1 D0 D1 DN
ddd=[-N -1 0 1 N];
A=spdiags(DD,ddd,N*M,N*M);

B=sparse(1,M*N);
l=1:N;
B(l)=Cmv;
clear l DD ddd;

X=A\B';

C=reshape(X,N,M);

z=0:dz:lcap;
r=0:dr:a;

% C - concentration in mobile phase [mole/cm^3]
% Fvac - permeating flux into vacuum [mole/sec]

% Results
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

Fvac=2*pi*D*K*dz*sum(C(N,2:M))/log(b/a); % permeating flux [mole/sec]
Fvac=full(Fvac);
sprintf('Permeating flux through capillary membrane into vacuum is %g mole/sec', Fvac)

hold off

figure(1)
mesh (z,r,C)
title('Concentration in mobile phase')
xlabel('z, cm')
ylabel('r, cm')
zlabel('Concentration, mole/cm^3')
axis([0 lcap 0 a 0 C(1,1)])

figure(2)
plot(z,C(M,:))
grid on
zoom on
title('Concentration in contacting layer of mobile phase')
xlabel('z, cm')
ylabel('Concentration, mole/cm^3')

figure(3)
for i=5:10:N
   plot(r,C(:,i))
   hold on
end
```

```
hold off
grid on
title('Concentration in different cross-sections of mobile phase')
xlabel('r, cm')
ylabel('Concentration, mole/cm^3')
axis([0 a*(1+0.1) 0 C(1,1)*(1+0.1)])
zoom on
toc
```

Mob_ns_demo.m

```
script

% This is a Matlab5 script file for simulation of analyte concentration
% redistribution in liquid mobile phase pumped through a lumen of a
% capillary membrane while other side of the membrane is exposed to vacuum.

% At every time step this script file calculates concentration profiles in
% mobile phase (two-dimensional problem C=C(r,z,t)). Parameters of experiment,
% initial concentration profile in mobile phase and time dependence of
% analyte concentration in inlet cross-section of mobile phase (scenario of
% analysis) are used as initial conditions.

% The data obtained can be used for simulation of nonsteady-state permeation
% from liquid phase through capillary membrane into vacuum.
% Note, that this code requires significant time resources for execution.
% That is why I recommend to use widely steady-state mobile phase concentration
% distribution (obtainable by mob_st_demo.m) and to use mob_ns_demo.m only for
% informative time intervals those corresponds to the processes of concentration
% redistribution in mobile phase.

% Written by Alexey A. Sysoev (alexey.sysoev@msl.mephi.ru) 18 Dec 1998
% Modified 18 Mar 2000

clear all

tic

% Defining parameters of the experiment
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
N=101; % Number of thickness (r) points
M=101; % Number of length (L) points
P=100; % Number of time points
dt=0.005; % time step [s]
Nav=6.022*10^23; % Avogadro constant
lcap=2.5;    % length of capillary 2.5 [cm]
a=0.0305/2;  % Inner radius [cm]
b=0.0635/2;  % Outer radius [cm]
Pt=75.8;       % Atmosphere pressure [cmHg]
Vm=18;         % Water molar volume [cm^3/mol]

V0=2*0.016; % Rate of pumping [cm^3/s]

D=4.9*10^-6;  % Diffusivity in membrane [cm^2/s]
Dm=7.5*10^-6; % Diffusivity in mobile phase [cm^2/s]
K=171.8;      % Phase distribution coefficient [(mole/cm^3)/(mole/cm^3)
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Defining scenario of analysis
Cmrel=1*10^-6; %Relative concentration of analyte [mole/mole]
```

```
Cmv=Cmrel/Vm; % Molar volume concentration [mol/cm^3]
Cmvt(1:P)=Cmv; % Molar volume concentration in inlet cross-section at every time step
[mol/cm^3]

% Initial concentration distribution in mobile phase
C0=[Cmv*ones(N,1);zeros(N*M-N,1)]; % Clear water in the lumen of membrane capillary
before analysis,

%C0=Cmv*ones(N*M,1); % Clear air in the lumen of membrane capillary before analysis
(instantaneous filling the volume by liquid)

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

dr=a/(N-1);
dz=lcap/(M-1);

pp=D/Dm*K/(a*log(b/a));

D0=sparse(N,M);
D0(1:N,1)=ones(N,1);
D0(1:N,M)=ones (N,1);
D0(1,2:M-1)=ones(1,M-2);
D0(N,2:M-1)=ones(1,M-2)+dr*pp;
r=[0:dr:a];
r=r(:);
r(N)=[];
r(1)=[];
D0(2:N-1,2:M-1)=repmat(-r/dr^2-r/(Dm*dt),1,M-2);
D0=D0(:);

D1=sparse(N,M);
D1(1,2:M-1)=-ones(1,M-2);
D1(2:N-1,2:M-1)=repmat(r/(2*dr^2)+1/(4*dr),1,M-2);
D1=D1(:);
D1=[0;D1];
D1(M*N+1,:)=[];

Dm1=sparse(N,M);
Dm1(N,2:M-1)=-ones(1,M-2);
Dm1(2:N-1,2:M-1)=repmat(r/(2*dr^2)-1/(4*dr),1,M-2);
Dm1=Dm1(:);
Dm1(1,:)=[];
Dm1=[Dm1;0];

DN=sparse(N,M);
f=2*V0/(Dm*pi*a^2)*r.*(1-r.*r/a^2);
clear r
DN(2:N-1,2:M-1)=repmat(-f/(4*dz),1,M-2);
DN=DN(:);
DN=[zeros(N,1);DN];
DN(N*M+1:N*M+N,:)=[];

DmN=sparse(N,M);
DmN(1:N,M)=-ones(N,1);
DmN(2:N-1,2:M-1)=repmat(f/(4*dz),1,M-2);
clear f
DmN=DmN(:);
DmN(1:N,:)=[];
DmN=[DmN;zeros(N,1)];
```

```
DD=[DmN Dm1 D0 D1 DN];
clear DmN Dm1 D0 D1 DN
ddd=[-N -1 0 1 N];
A=spdiags(DD,ddd,N*M,N*M);

clear l DD ddd;

Ctime=zeros(N,M,P);

for i=1:P

sprintf('step %d from %d',i,P)

B=sparse(N,M);
B0=C0(:);
Bm1=[0;B0];
Bm1(M*N+1,:)=[];
Bm1=reshape(Bm1,N,M);
B1=[B0;0];
B1(1,:)=[];
B1=reshape(B1,N,M);
BmN=[zeros(N,1);B0];
BmN(M*N+1:M*N+N,:)=[];
BmN=reshape(BmN,N,M);
BN=[B0;zeros(N,1)];
BN(1:N,:)=[];
BN=reshape(BN,N,M);
B0=reshape(B0,N,M);

r=[0:dr:a];
r=r(:);
f=2*V0/(Dm*pi*a^2)*r.*(1-r.*r/a^2);
kBm1=repmat(1/(4*dr)-r/(2*dr^2),1,M);
kB0=repmat(r/dr^2-r/(Dm*dt),1,M);
kB1=-repmat(r/(2*dr^2)+1/(4*dr),1,M);
kBmN=-repmat(f/(4*dz),1,M);
kBN=repmat(f/(4*dz),1,M);
B=Bm1.*kBm1+B0.*kB0+B1.*kB1+BmN.*kBmN+BN.*kBN;

clear Bm1 kBm1 B0 kB0 B1 kB1 BmN kBmN BN kBN

B(:,1)=Cmvt(i);
B(:,M)=0;
B(1,2:M-1)=0;
B(N,2:M-1)=0;

B=B(:);

C0=A\B;

Ctime(:,:,i)=reshape(C0,N,M);

end

clear A B C0

z=0:dz:lcap;
r=0:dr:a;

i=1:P;
Cm(i)=sum(Ctime(N,2:M,i))/(M-1);
```

```
% If flow rate dynamics should be monitored, use following line to write on disk
% concentration in contacting layer for following use by mem_ns_demo or other codes.
% Please, note that value of P and a time step in files mob_ns_demo and mem_ns_test
% should be the same
%save Cmtime Cm

% Results
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
figure(1)

hold off

for i=4:10:P
   plot(z,Ctime(N,:,i))
   hold on
end
grid
xlabel('z, cm')
ylabel('Concentration, mole/cm^3')
title('Concentration in contacting layer at different time steps')
hold on
zoom

toc
```