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.
% 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 processes of concentration
% redistribution in mobile phase.

% Written by Alexey A. Sysoev (alexey.sysoev@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;
% For mobile liquid phase array Cm(1:P) first should be calculated.
% Array Cm(1:P) can be downloaded 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);
  Dml=zeros(NN,1);
  Dml(1:NN-2)=-f(2:NN-1);
  DD=[Dml D0 D1];
  clear Dml D0 D1
  ddd=[-1 0 1];
  A=smdiags(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));
% 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
N*V=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]
P=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)]

Cm=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+1,:)=[];

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

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

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

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

X=A\B';

C=reshape(X,N,M);

z=0:dz:1cap;
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 1cap 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

% 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.

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% 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,

%CO=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=1cap/(M-1);

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

DO=sparse(N,M);
DO(1,1:N,1)=ones(N,1);
DO(1:N,M)=ones(N,1);
DO(1,N,M)=ones(1,M-2);
DO(N,2:M-1)=zeros(1,M-2)+dr*pp;

r=[0:dr:a];
r=r(:);
r(N)=[];
r(1)=[];
DO(2:N-1,2:M-1)=repmat(-r/dr^2-r/(Dm*dt),1,M-2);
DO=DO(:);

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,:)=[];

Dml=sparse(N,M);
Dml(N,2:M-1)=-ones(1,M-2);
Dml(2:N-1,2:M-1)=repmat(r/(2*dr^2)-1/(4*dr),1,M-2);
Dml=Dml(:);
Dml(1,:)=[];
Dml=[Dml;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,:)=[];
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(:,);
    B1=[0;B0];
    B1=M*N+1,:=[];
    B1=reshape(B1,N,M);
    B1=reshape(B1,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);
kBml=repmat(1/(4*dr^2)-r/(2*dr^2),1,M);
kB0=repmat(r/(2*dr^2)+1/(4*dr^2),1,M);
kBl=repmat(r/(2*dr^2),1,M);
kBmN=repmat(f/(4*dz),1,M);
kBn=repmat(f/(4*dz),1,M);
B=Bml.*kBml+B0.*kB0+B1.*kB1+BmN.*kBmN+BN.*kBn;

    clear Bml kBml 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:1cap;
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