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Lars Wadsö

Rapport TVBM-7128
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1 Nomenclature

The figures given refer to the SORP4 instumentation with water vapor at 25°C and 1 atm.

a	activity of vapor ($=p/p_{\text{sat}}$)	1
Δa	difference in activity over the sample	1
A_s	exposed surface area of sample ($130{\cdot}10^{-6}$)	m^2
c	vapor concentration in sample	g/m^3
C	vapor capacity of cell in simulation	g
D_p	diffusion coefficient in air with p as potential ($182{\cdot}10^{-9}$)	g/m/s/Pa
D_c	diffusivity in sample with c as potential	m^2/s
F	mass flow rate	g/s
$F_{\max}$	flux in vessel when activity difference is 1.0 ($400{\cdot}10^{-9}$)	g/s
h	sample thickness	m
k	vapor conductance between cells in simulation	g/s
L	dimensionless factor ($=h\alpha/D_c$)	1
M	dry mass of sample	g
n	number of simulation cells in sample	1
p	vapor pressure	Pa
p_{sat}	saturation vapor pressure (3160)	Pa
R	flow resistance ($1/k$)	s/g
t	time	s
v_{sat}	vapor content of air (23.0)	g/m^3
V	volume	m^3
α	mass transfer coefficient	m/s
δ	ratio of diffusion coefficients D_p in sample and in air	1
λ	dimensionless length	1
ξ	dimensionless slope of isotherm ($\partial c/\rho/\partial a$)	1
ρ	density of dry sample	g/m^3
τ	dimensionless time	1

2 Introduction

In the SORP4 sorption microcalorimeter a sample is scanned in vapor concentration from low to high values. During this process there will be a gradient through the sample. This report describes two ways of finding out how large this gradient is (expressed as difference in activity (Δa) between top and bottom of the sample). The reader is refered to Wadsö and Wadsö (1996, 1997) for a description of the experimental technique.

3 Analytical solution

The arrangement in the SORP4 vessel can be seen as a vapor source, a mass transfer coefficient (the gas phase in the tube), and a sample. The concentration or activity as a function of time and position in such a system can be solved analytically. There are three differences between such a solution and the actual case:

1. The vapor capacity of the gas phase is not taken into account. As the vessel is modelled as a flow resistance without vapor capacity the solution will give a too rapid sorption at the beginning of a measurement (cf. Appendix A).
2. The three dimensional geometry of the vessel is cannot be taken into account.
3. The sorption isotherm must be linear in the analytical solution. The slope of the sorption isotherm is $\xi\rho$, i.e. the activity $a = 1$ corresponds to a concentration $\xi\rho$ g/m^3.

The density of a sample in SORP4 may be found from the following relation:

$$\rho = \frac{M}{A_s h} \tag{1}$$

We introduce a mass transfer coefficient α of the gas phase as:

$$\frac{F}{A_s} = \alpha \Delta c \tag{2}$$

The flow rate per unit area is α times the concentration difference over the gas phase (i.e. between the exposed surface of the sample and the water source; the concentration of the latter is taken as $\xi\rho$). For the present case α may be found from the following equation:

$$\frac{F_{\max}}{A_s} = \alpha\xi\rho \tag{3}$$

Here, both flow rate and concentration difference is taken at the conditions of maximum flow rate. Note that $\xi\rho$ is the concentration difference corresponding to an activity difference of 1.0, i.e. the situation in which $F_{\max}$ was measured. The exposed sample surface (A_s) must be introduced because α in Eq. 3 is defined per unit area perpendicular to the flow (the unit m/s for α is actually an abbreviation of g/s/m^2/(g/m^3))

The ratio of the flow resistance of the sample and the flow resistance of the gas phase is:

$$L = \frac{h\alpha}{D_c} \tag{4}$$

Crank (1975) gives the following solution (in my notations) for the concentration in a plane sheet ($-h \leq x \leq h$) with a mass transfer coefficient α on its surfaces:

$$\frac{c(\lambda, \tau)}{\xi} = 1 - \sum_{n=1}^{\infty} \frac{2L\cos(\beta_n\lambda)\exp(-\beta_n^2\tau)}{(\beta_n^2 + L^2 + L)\cos\beta_n} \tag{5}$$

Here

$$\lambda = x/h \tag{6}$$

$$\tau = D_c t/h^2 \tag{7}$$

and the β_ns are the positive roots of

$$\beta \tan\beta = L \tag{8}$$

The left hand side of Eq. 5 has been simplified from the equation given by Crank because in our case the final concentration after infinite time equals ξ and the initial concentration is 0. The exposed surface is at $x = h$ ($\lambda = 1$) and the unexposed bottom surface is at $x = 0$ ($\lambda = 0$)

A problem in applying this solution to the present case is that we have to express the transport properties of both the sample and the gas phase with concentration (in the sample) as potential. Equation 3 takes care of this problem for the gas phase. For the sample diffusivity the following relation is used:

$$D_c = \delta D_p \frac{\partial p}{\partial a}\frac{\partial a}{\partial c} = \delta D_p p_{\mathrm{sat}} \frac{1}{\rho\xi} \tag{9}$$

Here, the transport property of the sample is expressed as a hinderance factor δ (the ratio of the flow through a sample and through still air under the same vapor pressure gradient).

To find the size of L we use Eqs. 4, 3 and 9 and write:

$$L = \frac{h\alpha}{D_c} = \frac{hF_{\max}\rho\xi}{A_s\rho\xi\delta D_p p_{\text{sat}}\rho\xi} = K\frac{h}{\delta} \tag{10}$$

$$K = \frac{F_{\max}}{A_s D_p p_{\text{sat}}} \tag{11}$$

In the present case

$$\begin{aligned} K &= 5.345\ \text{m}^{-1} \\ 0.5\ \text{mm} &\leq h \leq 3\ \text{mm} \\ 0.1 &\leq \delta \leq 1.0 \end{aligned} \tag{12}$$

This gives the following bounds for L:

$$0.003 \leq L \leq 0.2 \tag{13}$$

It is seen that L is quite small, i.e. the flow resistance in the gas phase is high compared to the flow resistance in the sample, and this is the way that the SORP4 instrument is to work; with the gas phase governing the rate of sorption.

As a measure of the activity gradient over the sample we take the difference in activity $a(\lambda, \tau)$ between the sample surface ($\lambda = 1$) and the bottom ($\lambda = 0$) of the sample:

$$\Delta a(\tau) = a(1, \tau) - a(0, \tau) \tag{14}$$

As $a = c/\rho/\xi$ Eq. 5 may be written as:

$$\Delta a(\tau) = 2L \sum_{n=1}^{\infty} \frac{(\cos\beta_n - \cos 0)\exp(-\beta_n^2\tau)}{(\beta_n^2 + L^2 + L)\cos\beta_n} \tag{15}$$

For $\tau > 0.3$ the terms for $n \geq 3$ will be very small and may be safely neglected (the worst case is for n=3, τ=0.3 and L=0.2 when $\exp(-\beta_n^2\tau) < 10^{-5}$ and the denominator $(\beta_3^2 + L^2 + L)\cos\beta_3 > 40$).

The βs are troublesome to work with but must be found with more than three correct decimals for the solutions to be good. With only two terms the solution may be written as:

$$\Delta a = 2L\left[\frac{(\cos\beta_2 - 1)\exp(-\beta_2^2\tau)}{(\beta_2^2 + L^2 + L)\cos\beta_2} + \frac{(\cos\beta_1 - 1)\exp(-\beta_1^2\tau)}{(\beta_1^2 + L^2 + L)\cos\beta_1}\right] \tag{16}$$

This equation gives the difference in activity over the sample as a function of time for different values of L.

4 Computer simulation

I have also modelled the SORP4 vessel and the sample as a one dimensional series of vapor capacitances (C) connected by conductances (k). Each capacitance cell has an activity (a) and between capacitances there are vapor flows (F). For the cells in the sample the concentration can be calculated from the activity by the sorption isotherm (which is a piece-wise linear function in our simulation).

There are two differences between such the computer simulation and the actual case:

1. The three dimensional geometry of the vessel is simplified in the one dimensional solution.
2. The problem is discretized. This is no problem, however , as the discretization can be made very fine.

Figure 1 shows the model. The gas phase is modelled as five capacitances and the sample is modelled as n capacitances. The numbering of the capacitances and the conductances is given in Fig. 1 for the case when n is 4. The capacitance C_{n+7} (the last capacitance C_{11} in Fig. 1) is a dummy capacitance to speed up the simulation (as the conductance k_{n+6}=0 there will never be any flow to C_{n+7}). There is also a capacitance C_1 which has a similar purpose: its activity is a_1=1.0 at the start of the simulation, but as the simulation program never changes its value it will act as a constant activity vapor source.

The following equations together with Fig. 1 give the simulation procedure:

$$F_i = k_i(a_{i+1} - a_i) \tag{17}$$

$$\Delta a_i = \frac{F_i - F_{i+1}}{C_i}\Delta t \tag{18}$$

Here, Δt is the time step in the simulation which is made with the forward difference method. For each time step the flows F between the cells are first calculated; then the resulting changes in the activities Δa are computed. The time step must be chosen according to the following criterion to get a stable solution (Eftring 1990):

$$\Delta t \leq \min(\frac{C_i}{k_{i-1} + k_i}) \tag{19}$$

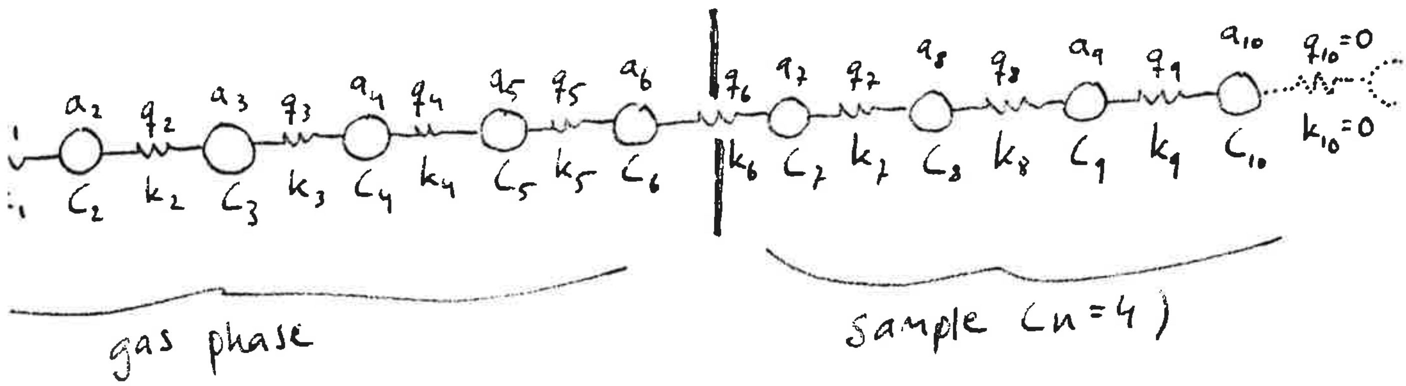


Figure 1: The simulation model with four sample cells (n=4). The boundary between the gas phase and the sample is shown as a thick vertical line.

To calculate the conductances the following general relations were used:

$$\begin{aligned} \text{gas phase:} \quad & k = \frac{F}{\Delta a} \\ \text{sample:} \quad & k = \frac{\delta D_p p_{\text{sat}} A_s}{h/n} \end{aligned} \tag{20}$$

For the gas phase a steady-state computer simulation was used to find the Δa:s over five quite arbitrarily chosen parts of this phase. For the sample Eq. 20 gives the conductivity of a sample cell of thickness h/n and surface area A_s.

The capacitances to be used in the simulation were calculated with:

$$\begin{aligned} \text{gas phase:} \quad & C = v_{\text{sat}} V \\ \text{sample:} \quad & C = \xi \rho V \end{aligned} \tag{21}$$

The capacities are calculated as the vapor content of a cell when a=1.

The full calculation procedure is given in some detail below:

1. A steady-state computer simulation was made of the activity gradients within an empty vessel with $a = 1$ at the bottom (vapor source) and $a = 0$ at the top (vapor sink). The vessel was then divided into five parts as shown in Fig. 2a. The values of a^{sim}(explained in Fig. 2), V_a and V_b were:

$$\begin{aligned} a^{\text{sim}} &= 0.105 \\ V_a &= 0.72 \cdot 10^{-6}\ \text{m}^3 \\ V_b &= 1.43 \cdot 10^{-6}\ \text{m}^3 \end{aligned}$$

2. To simplify the calculation it was made with resistances R (the inverses of k). Figure 2 shows how the vessel is divided into five parts, and how resistances (R_a:s and R_b:s) connect the center of each cell with a boundary between two cells. It should be noted that the tube part of the vessel is divided into four equal parts so that the eight R_a:s are equal and that the mid-point of the top part of the vessel (the chamber) is chosen so that the resistances from the mid-point to each boundary are equal.

3. The simulation gave that $a^\mathrm{sim} = 0.105$ (64 mm from the bottom of the tube, cf. caption to Fig. 2). The resistance R_a is then calculated as

$$R_\mathrm{a} = \frac{1.00 - a^\mathrm{sim}}{8F^\mathrm{max}} \tag{22}$$

4. The resistance R_b may be calculated in a similar fashion:

$$R_\mathrm{b} = \frac{a^\mathrm{sim} - 0.00}{2F^\mathrm{max}} \tag{23}$$

5. The conductances are then calculated according to the following equations:

$$\begin{aligned} k_1 &= \tfrac{1}{R_\mathrm{a}} \\ k_i &= \tfrac{1}{2R_\mathrm{a}} \quad \text{for } 2 \leq i \leq 4 \\ k_5 &= \tfrac{1}{R_\mathrm{a}+R_\mathrm{b}} \\ k_6 &= \tfrac{1}{R_\mathrm{b}+R_\mathrm{c}} \end{aligned} \tag{24}$$

   where R_c is calculated below.

6. The conductances in the sample are calculated in a similar fashion as those in the gas phase. The resistance R_c is defined as (cf. Fig 3b):

$$R_c = \frac{h}{2n\delta D_p p_\mathrm{sat} A_\mathrm{s}} \tag{25}$$

   The conductances are then calculated as:

$$k_i = \tfrac{1}{2R_\mathrm{c}} \quad \text{for } 7 \leq i \leq (5+n) \tag{26}$$

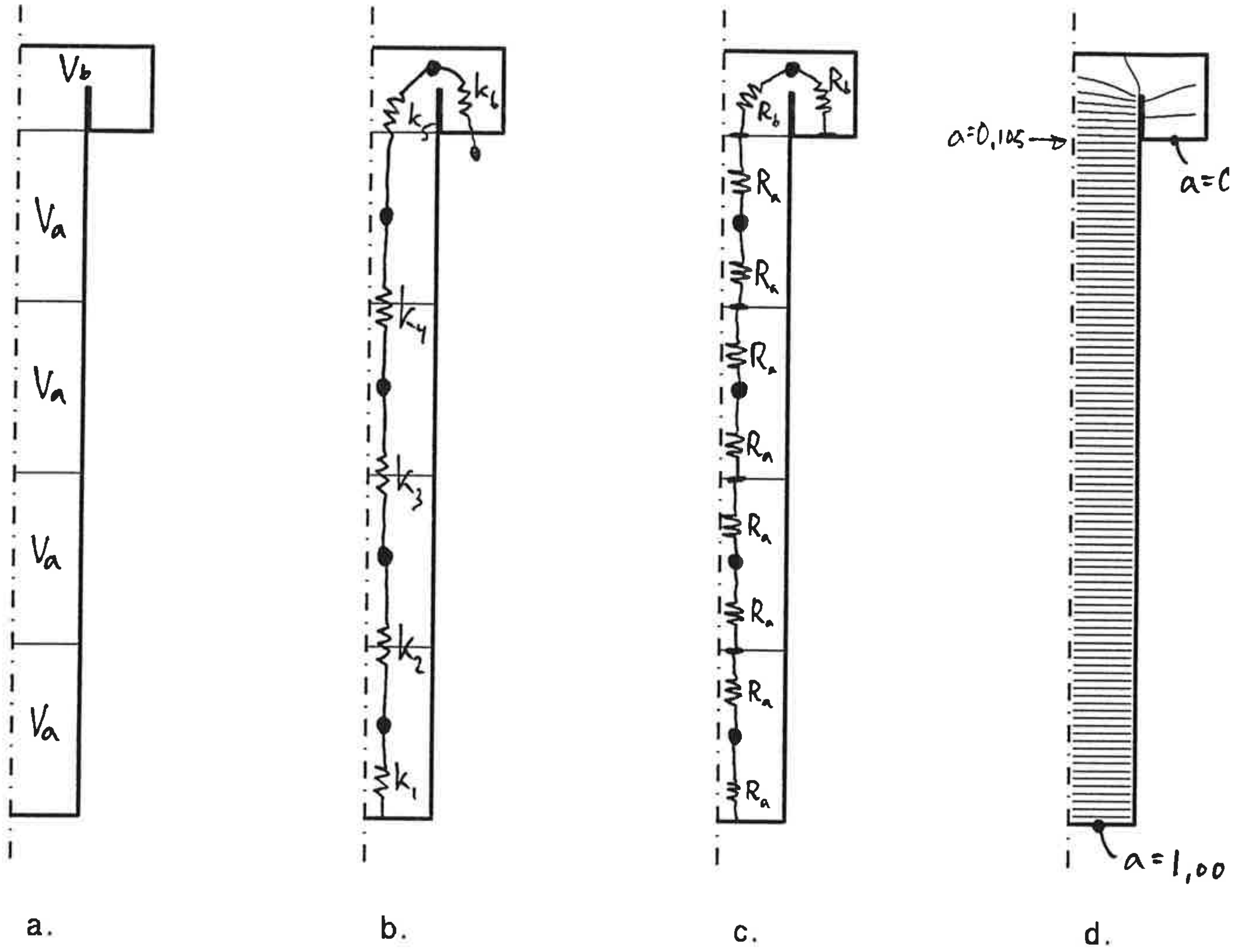


Figure 2: The simulation model of the gas phase. a. The five volumes corresponding to the five capacitances in the gas phase. b. The conductancies in the gas phase. c. The resistances in the gas phase used to calculate the conductancies. d. The iso-activity lines in the gas phase when there is an activity potential of 1.00 over the vessel. The arrow marks the boundary between two of the volumes (cf. Fig. 2a) where the activity is 0.105.

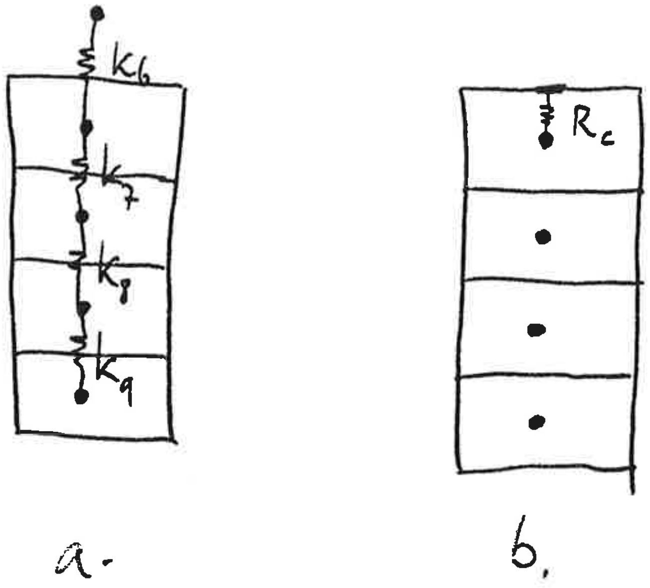


Figure 3: The simulation model of the sample. a. The conductanses. b. The resistance Rc used in the calculation of the conductance k6.

7. The capacities in the vapor phase are calculated as:

$$\begin{aligned} C_i &= v_{\mathrm{sat}} V_{\mathrm{a}} \quad \text{for } 2 \leq i \leq 5 \\ C_6 &= v_{\mathrm{sat}} V_{\mathrm{b}} \end{aligned} \tag{27}$$

8. The capacities in the sample were calculated as:

$$C_i = \xi \rho \frac{h}{n} A_s \text{ for } 7 \leq i \leq (6 + n) \tag{28}$$

   The simulations were made with a MATLAB program sorp4sim.m that is given in Appendix B.

The activity difference Δa was calculated by multiplying the activity difference between the top and bottom cell of the sample by $\frac{n}{n-1}$ thus correcting for the fact that the activities calculated by the simulation are in the cell centers, not at the boundaries. This correction is very good for the type of activity gradient one will get in a sample in SORP4.

5 Results from calculations and simulations

Figure 4 gives the results of analytical calculations of Δa as a function of dimensionless time τ for different values of L within the bounds given in Eq.13. In Appendix B are five examples of simulations and calculations of

Δa for the same input values. The agreement is very good, indicating that the two different ways of solving the problem have been applied successfully. All simulations were made with five sample cells. Other tests have also shown that the simulation gives correct values of $a(\lambda, \tau)$.

6 References

Crank, J. (1975) The Mathematics of Diffusion, Oxford University Press

Eftring, B. (1990) Numerical calculation of thermal processes (in Swedish), Swedish Building Research Council, Stockholm, R81:1990

Wadsö, I. and Wadsö, L. (1996), Thermochim. Acta, 273 277-

Wadsö, I. and Wadsö, L. (1997), J. Thermal Anal., 49 1045-1052

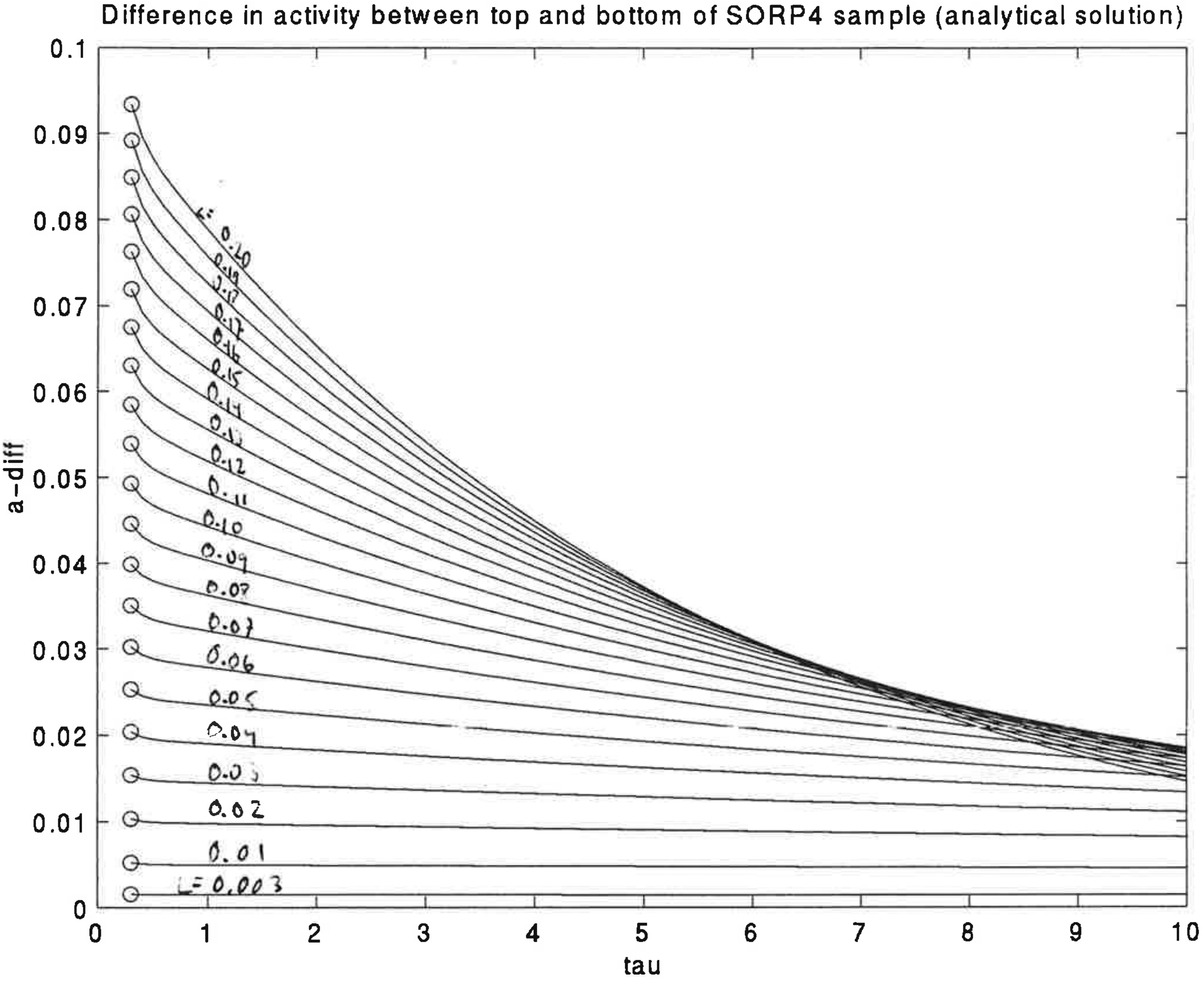


Figure 4: The analytical solution for the activity difference as a function of dimensionless time and L. The bottom curve is for L=0.003; the others are for (from bottom to top) L=0.01 to 0.2 in steps of 0.01.

7 Appendix A: Five comparisons between the two solutions

Appendix A contain the results of five comparisons of results from the analytical solution and the computer model. In all cases the agreement between the two methods is very good when τ is greater than 0.5.

Fig. 11.

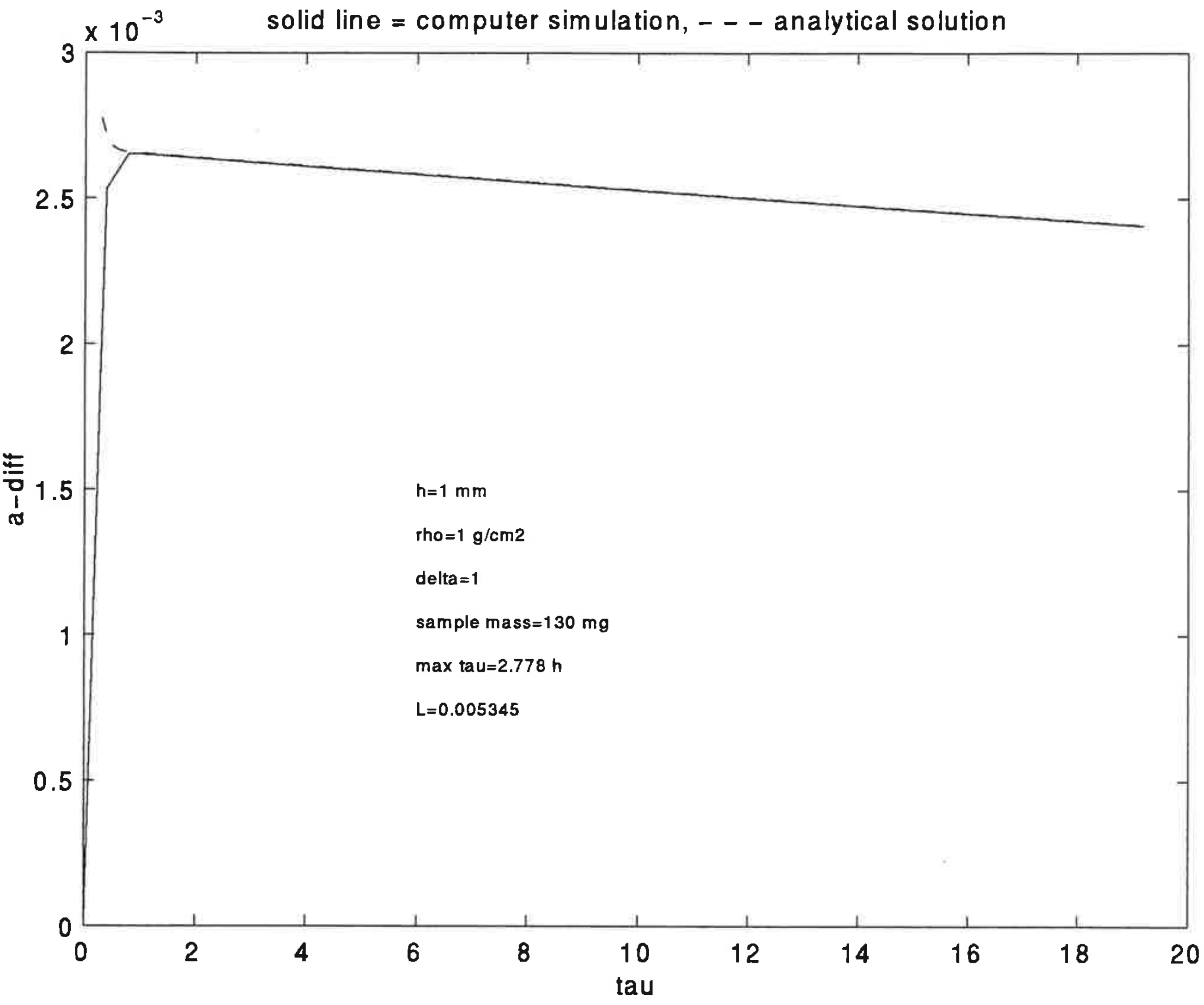

solid line = computer simulation, – – – analytical solution
x 10^-3
3
2.5
2
1.5
1
0.5
0
a–diff
0
2
4
6
8
10
12
14
16
18
20
tau
h=1 mm
rho=1 g/cm2
delta=1
sample mass=130 mg
max tau=2.778 h
L=0.005345

Fig. 12

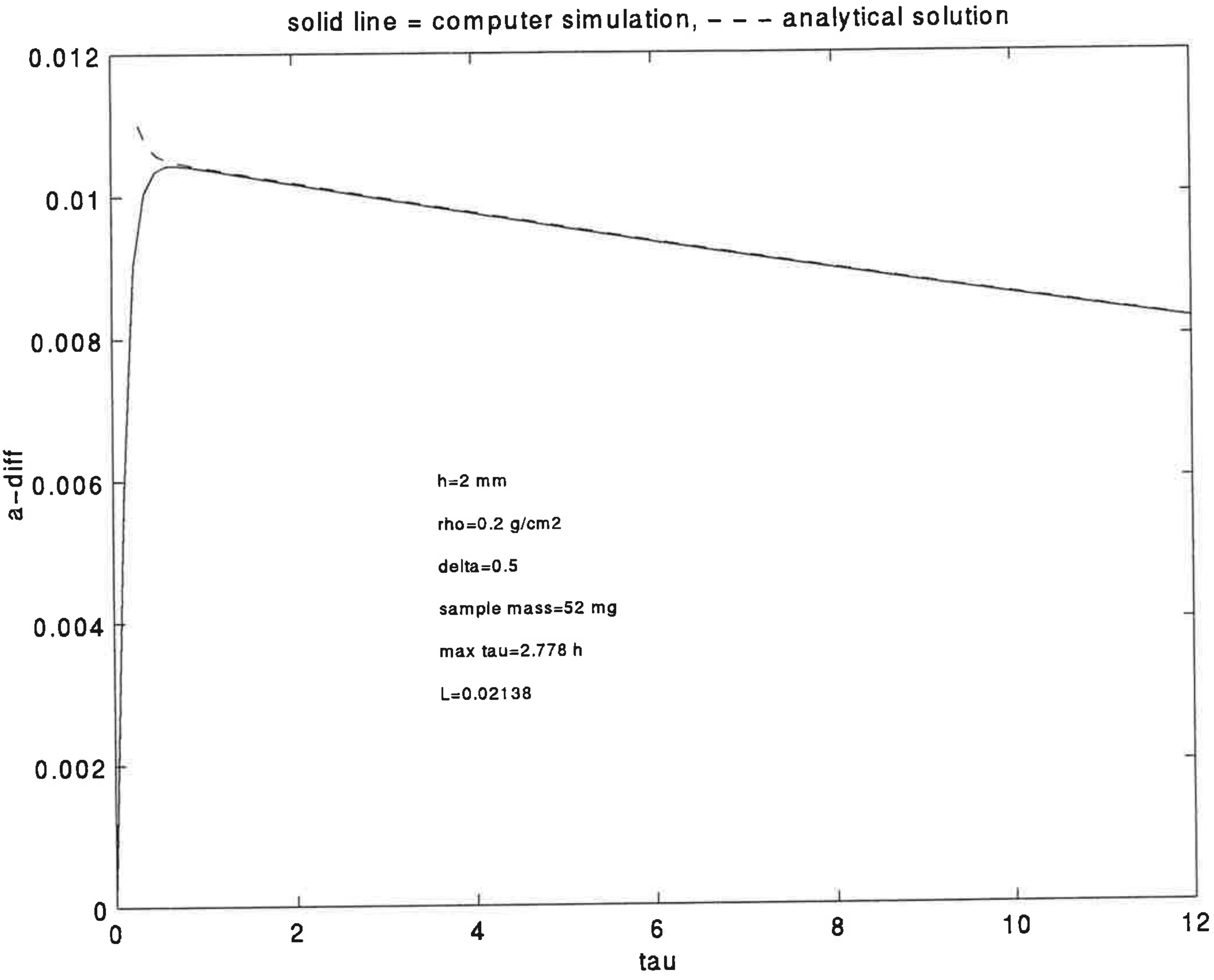

solid line = computer simulation, - - - analytical solution
0.012
0.01
0.008
0.006
0.004
0.002
0
a-diff
0
2
4
6
8
10
12
tau
h=2 mm
rho=0.2 g/cm2
delta=0.5
sample mass=52 mg
max tau=2.778 h
L=0.02138

Fig. 13

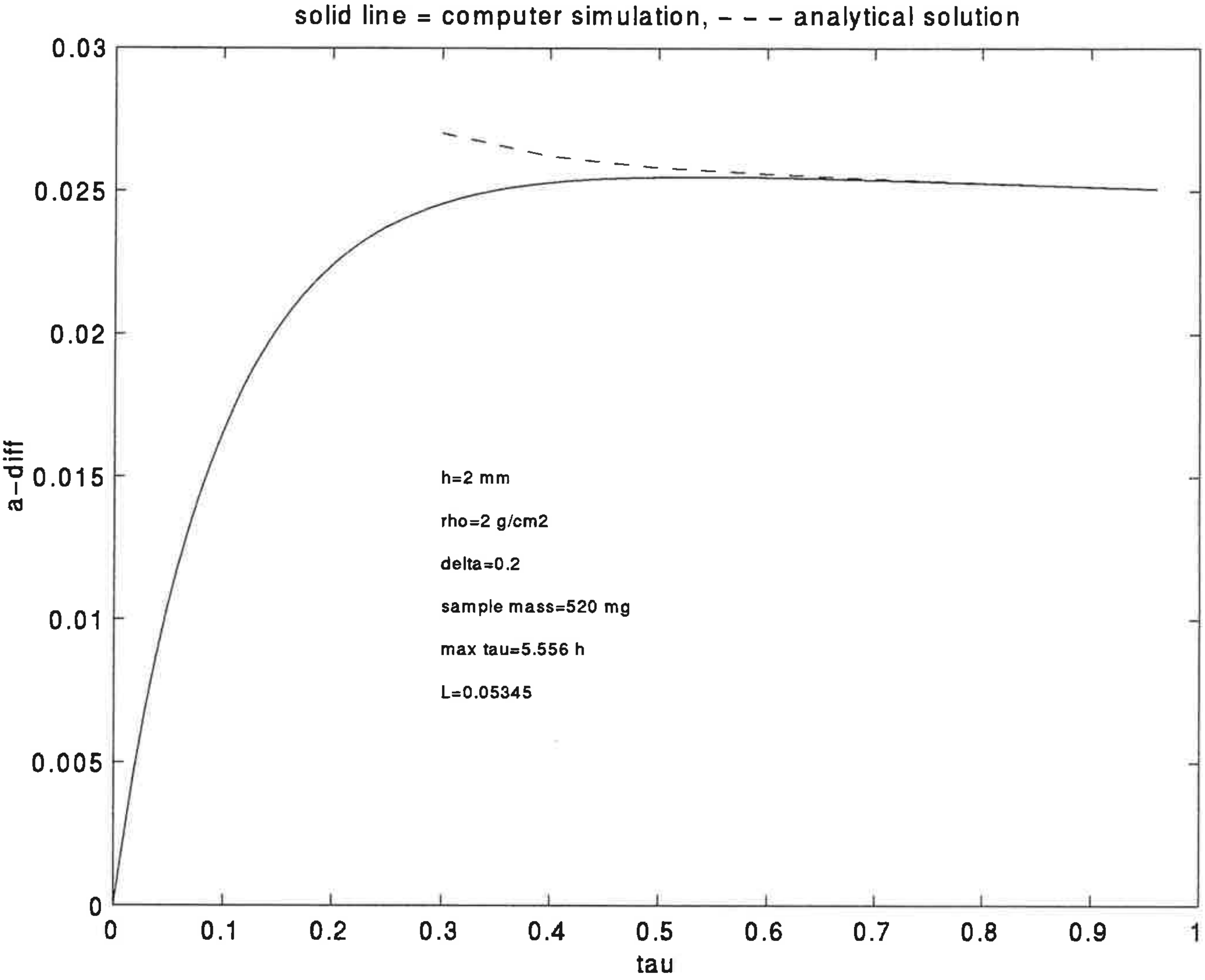

solid line = computer simulation, - - - analytical solution
a-diff
0.03
0.025
0.02
0.015
0.01
0.005
0
tau
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
h=2 mm
rho=2 g/cm2
delta=0.2
sample mass=520 mg
max tau=5.556 h
L=0.05345

Fig. 14

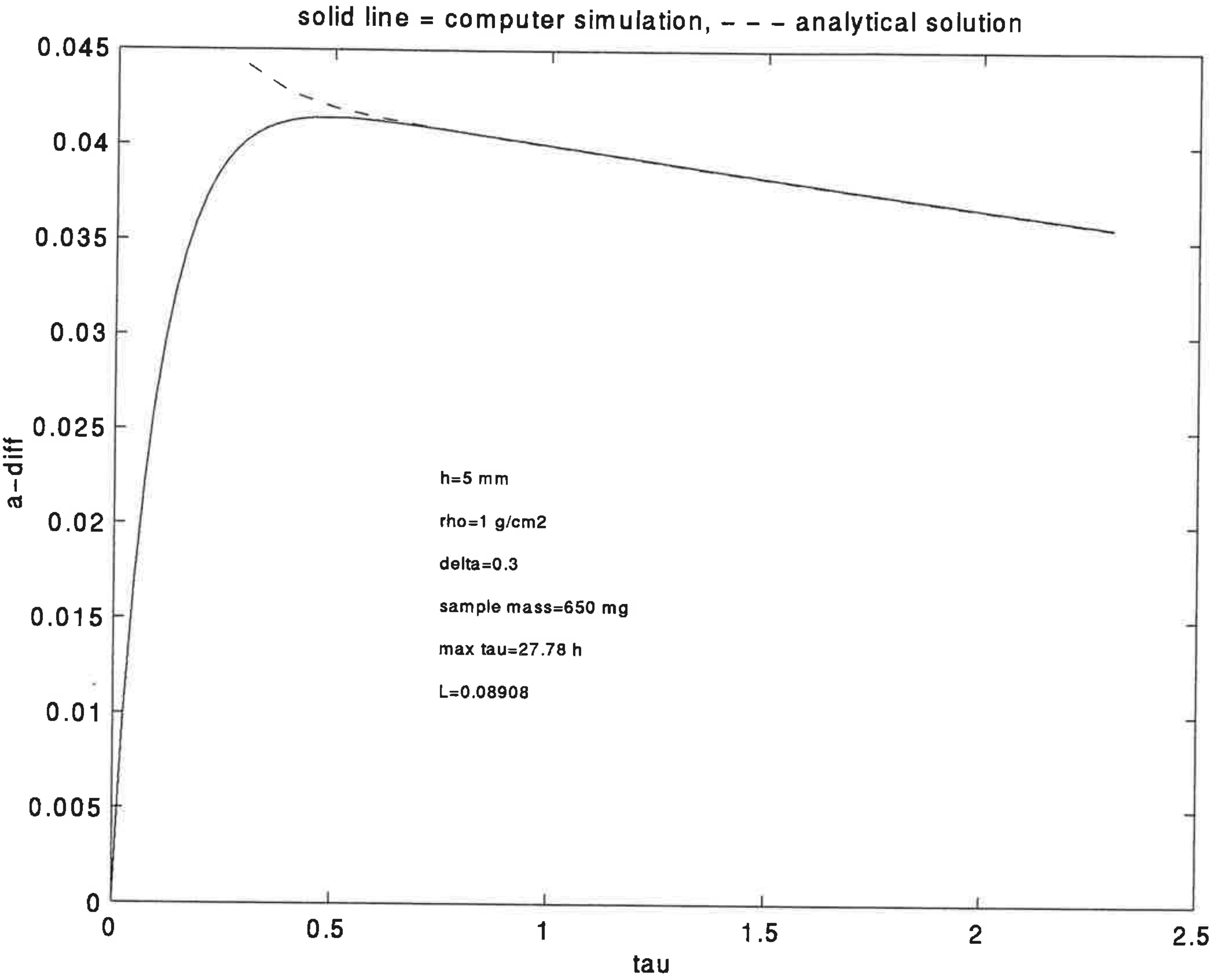
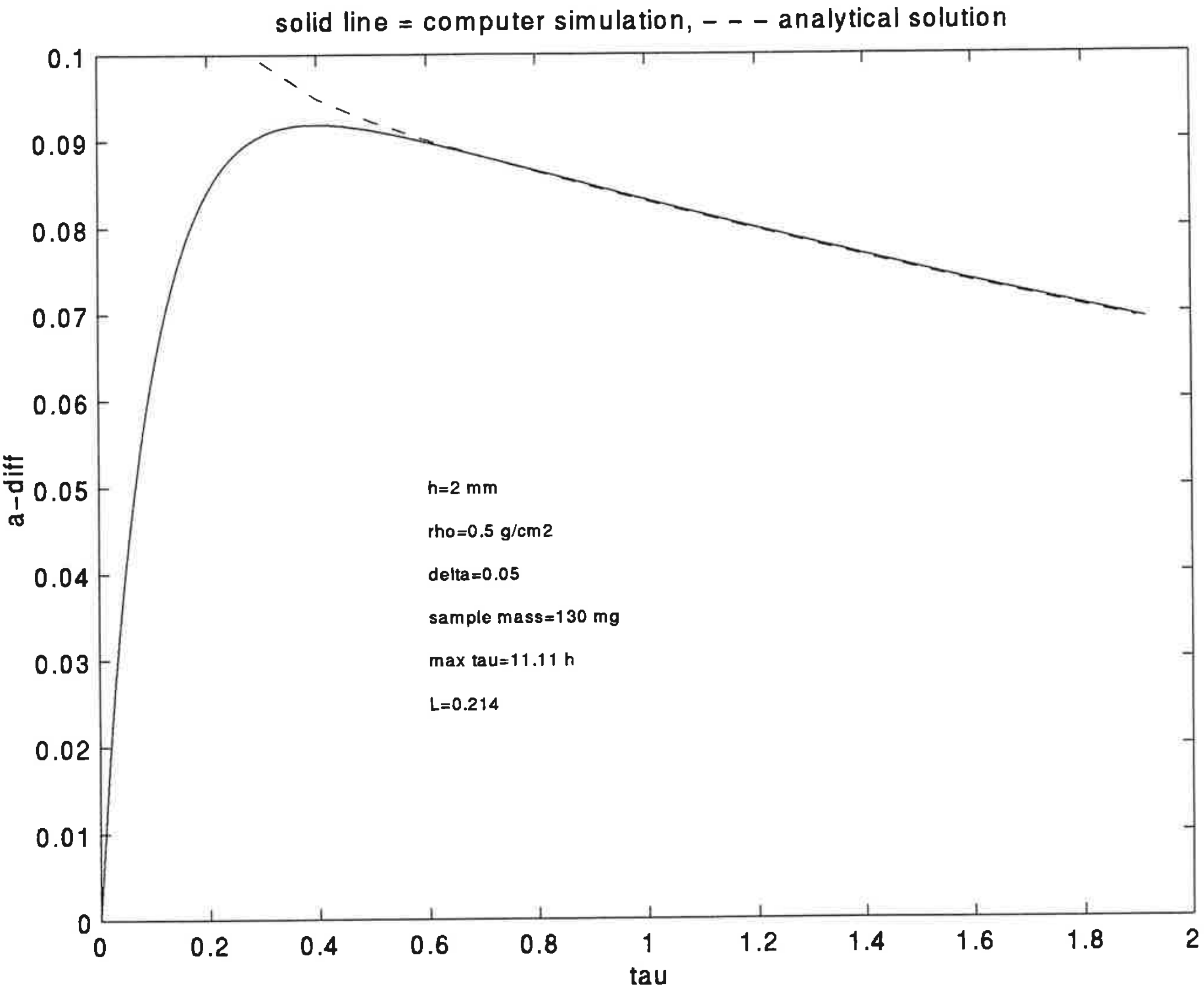

solid line = computer simulation, - - - analytical solution
a-diff
0.045
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
tau
0
0.5
1
1.5
2
2.5
h=5 mm
rho=1 g/cm2
delta=0.3
sample mass=650 mg
max tau=27.78 h
L=0.08908

Fig. 45


solid line = computer simulation, - - - analytical solution
a-diff
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.1
tau
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
h=2 mm
rho=0.5 g/cm2
delta=0.05
sample mass=130 mg
max tau=11.11 h
L=0.214

8 Appendix B: The simulation program and other programs used in this study

```
%    sorp4sim - a one-dimensional simulation of
%    the vapor transport and sorption in SORP4
%
% This MATLAB 4 program simulates a measurement with the sorption microcalorimeter
% SORP4 (not the sorption enthalpies...). The following input is asked for by the program:
%               h                           height of the sample (mm)
%               rho                         density of the sample (mg)
%               delta                       ratio of the diff.coeffs in sample and in air
%               n                           number of calculation layers in sample
%               tend                        end of simulation (s)
%               tout                        time interval between outputs (s)
% If you give no input the following standard input will be used:
% h=2 mm, rho=0.15 g/cm3, delta=0.5 (M=37 mg), n=5, tend=20000, tout=200, linear isotherm.
%
% It is also possible for the user to make other changes in the program:
%               vsat, psat, Dpair           properties of vapor in air
%               As                                  surface area of sample (m2)
%               Dvh                                 vaporization enthalpy (J/g)
%               aiso, ciso                  sorption isotherm
%               C, k                                capacities & conductancies of model
%               a(1)                                activity at vaporization surface
% A simulation gives the following numerical ouput (+a number of plots):
%               t           time (s)    [a vector]
%               a           activity in each computational cell (1)          [a matrix]
%               Da          the activity difference over the sample (1)
%               c           mean concentration in sample (kg/kg)   [a vector]
%               Pv          thermal power of vaporization (W)   [a vector]
% The following points should be noted:
%               - The simulation is by simple forward differences (Fick's law and mass
%                 balances are calculated in small time increments). The time step dt is
%                 automatically calculated as the maximum time step found in any part of the
%                 model during the whole simulation (the program would have a higher speed
%                 if dt was continously changed, but this is not trivial to implement)
%               - During the simulation t, a and c are used and the output is stored in
%                 tt, aa and cc. After the simulation the result is transferred to
%                 t, a and c. The thermal power of vaporization is given in Pv.
%               - Calculations are made with SI-units: kg, m, s, Pa
%               - Standard temperature is 25oC and the vapor forming liquid is water
%               - For each cell only the activity (a) is saved, but as equilibrium is
%                 assumed the vapor concentration can be found with the sorption isotherm
%
%               Lars Wadsö 970522 970527 970814 970820

%--------------------user input--------------------
As=130e-6; %exposed surface of sample (m2)
h=input('height of sample (mm) :');
if (h==0)|(h==[]);h=2;end %standard case
h=h/1000; %into units of m
rho=input('density of sample (g/cm3) :');
if (rho==[])|(rho==0);rho=0.15;end %standard case
rho=rho*1000; %into kg/m3
delta=input('Dp(sample)/Dp(air) :'); %delta=ratio of diff. coeff.
if (delta==0)|(delta==[]);delta=0.5;end %standard case
M=h*As*rho;
disp(' ');
disp(['Sample mass = ',num2str(M*1e6),' mg']);
n=input('number of calculation layers in sample :');
if (n==0)|(n==[]);n=5;end; %standard case
```

```
tend=input('end of simulation (s) :');
if (tend==0)|(tend==[]);tend=20000;end %standard case
tout=input('time interval between outputs (s) :');
if (tout==0)|(tout==[]);tout=200;end
%--------------------physical data------------------
vsat=23e-3; %vapor content (kg/m3)
psat=3160; %vapor pressure (Pa)
Dpair=182e-12; %diffusion coefficient of water vapor in air (kg/Pa/m/s)
As=130e-6; %cross sectional area of sample (m2)
Dvh=2440e3; %heat of vaporization (J/kg)
Fmax=400e-12; %maximal vapor flow (kg/s)
%--------------------sample data--------------------
isotype=input('type of isotherm ? (1=linear, 2=sigmoid, 3=hydrate) :');
%aiso are the activity knickpoints on isotherm
%ciso are the concentration knickpoints on isotherm (kg/kg)
if (isotype==0)|(isotype==[]);isotype=1;end %standard case
if isotype==1 %linear
  aiso=[0 1];ciso=[0 0.3];
elseif isotype==2 %sigmoid (wood Eucalyptys regnans, Christensen & Kelsey 1959)
  aiso=[0 0.05  0.10  0.40  0.70 0.80 0.90 0.95 1.00];
  ciso=[0 0.02  0.035 0.085 0.15 0.18 0.23 0.27 0.37];
elseif isotype==3 %hydrate (Morphine sulphate)
  aiso=[0 0.029   0.031   0.229   0.231  0.95  1.0];
  ciso=[0 0.0001  0.0538  0.0539  0.135  0.136 0.2];
end
xi=diff(ciso)./diff(aiso); %slope of isotherm
%--------------------show input--------------------
figure(1);clf
subplot(121)
plot(aiso,ciso,'*');hold on;plot(aiso,ciso,'-');hold off
xlabel('relative activity')
ylabel('vapor content (kg/kg)')
subplot(122)
text(0,5,['sample density=',rho,' kg/m3']);
text(0,4,['sample height=',num2str(h*1000),' mm']);
text(0,3,['sample mass=',num2str(M*1e6),' mg']);
text(0,2,['diff.ratio=',num2str(delta)]);
text(0,1,[int2str(n),' simulation cells']);
text(0,0,['simulation ends at ',num2str(tend),' s']);
text(0,-1,['output interval: ',num2str(tout),' s']);
axis([-1 10 -2 5]);set(gca,'Visible','Off')
disp('Press any key to continue (Ctrl-c to abort)')
pause
%--------------------simulation data---------------
Va=0.72e-6;Vb=1.43e-6;
asim=0.105;
Ra=(1-asim)/8/Fmax;Rb=asim/2/Fmax;Rc=h/2/n/delta/Dpair/psat/As;
k(1)=1/Ra;
k(2:4)=ones([1 3])/2/Ra;
k(5)=1/(Ra+Rb);
k(6)=1/(Rb+Rc);
k(7:5+n)=ones([1 n-1])/2/Rc;
k(6+n)=0;
C(1)=0;
C(2:5)=ones([1 4])*Va*vsat;
C(6)=Vb*vsat;
C(7:6+n)=ones([1 n])*h/n*As*xi(1)*rho;
```

```
%--------------------simulation initialization------
nn=n+5; %number of last active conductance in sample
a=zeros([1 nn+1]); %activities
a(1)=1; %activity of water
q=zeros([1 nn+1]); %flows (kg/s)
Q=0; %Q keeps track of the flow into the sample since last output (kg/s)
dt=min([C(2:6)./(k(1:5)+k(2:6))]); %max time step in vapor phase
for z=1:length(xi)
  dt=min([dt M/n*xi(z)*ones([1 nn-6])./(k(6:nn-1)+k(7:nn))]); %max. time steps in sample
end
%dt=min([C(2:6)./k(1:5) C(2:6)./k(2:6)]); %max time step in vapor phase
%for z=1:length(xi)
%  dt=min([dt M/n*xi(z)*ones([1 nn-6])./k(6:nn-1) ...
%     M/n*xi(z)*ones([1 nn-6])./k(7:nn)]); %max. time steps in sample
%end
dt=dt*0.4; %to be on the safe side (0.5 is limit)
t=0; %time in simulation (s)
amax=aiso(length(aiso)); %maximal possible activity
amaxend=0; %when amaxend=1 the simulation has to be stopped
toutnext=tout; %second output time (first is at t=0)
leg=ones([1 n]); %part on isotherm in which each sample part is at each time
out=1; %counter for outputs
nout=ceil(tend/tout)+1; %approx. no of outputs
tt=zeros([nout 1]); %in tt the sim. time is saved
aa=zeros([nout nn+1]); %in aa the activities are saved
aa(1,1)=1; %activity of source=1 from t=0
cc=zeros([nout 1]); %in cc the concentrations are saved
Da=zeros([nout 1]); %in Da the activity difference over the sample is saved
Pv=zeros([nout 1]); %in Pv the thermal power of vap. are saved
konst=1.05*dt/C(7); %to make the simulation run faster
%--------------------simulation--------------------
while (t<tend)&(amaxend==0)
  t=t+dt; %increment time
  q(1:nn)=(a(1:nn)-a(2:nn+1)).*k(1:nn); %calculate flows
  if a(7)+konst*(q(6)-q(7))>amax %stop before going outside defined isotherm in the first cell
    amaxend=1;
  end
  Q=Q+q(6); %add flow rate into sample to Q
  a(2:nn+1)=a(2:nn+1)+dt*(q(1:nn)-q(2:nn+1))./C(2:nn+1); %calculate activities (q(nn+1)==1)
  ind=findstr(a(6:6+n-1)>aiso(leg+1),'1'); %find index of sample cells that has changed leg on isotherm
  if ind~=[];
    leg(ind)=leg(ind)+1; %new leg
    C(ind)=M/n*xi(leg(ind)); %new capacity
  end
  if toutnext<t %time for output?
    out=out+1; %index in output vectors
    tt(out)=t; %output time
    aa(out,1:nn+1)=a(1:nn+1); %output activities
    Da(out)=(a(7)-a(nn+1))*n/(n-1); %difference in activity over sample
    cc(out)=cc(out-1)+Q*dt/M; %output mean concentration in sample
    Q=0; %zero Q
    Pv(out)=q(1)*Dvh; %output thermal power (W)
    toutnext=toutnext+tout; %time for next output
  end
end
%-----------------------cleaning up-------------------
L=length(tt); %L=length of vectors
if out<L %if the outputs have not filled the vector
```

```
  aa(:,out+1:L)=[]; %clear the unused parts of aa, cc, Pv, tt
  cc(out+1:L)=[];
  Pv(out+1:L)=[];
  tt(out+1:L)=[];
end
a=aa;c=cc;t=tt; %output is in t, a, c (&Pv)
clear aa cc tt %clear the simulation var. to save space
%-------------------------plot result--------------------
figure(2);clf
subplot(121) %plot of activities as function of time
col='rgggggyyyyyyyyyyyyyyy'; %water=red; gas phase=green; sample=yellow
for z=1:7+n-1
  eval(['plot(t,a(:,z),',"",col(z),"",')'])
  hold on
end
xlabel('time / s')
ylabel('activity')
subplot(122) %plot of thermal power as a function of time
plot(t,Pv*1e6)
xlabel('time / s')
ylabel('Thermal power of vaporization / uW')
hold off
figure(3);clf
subplot(121)
plot(t,Da)
xlabel('time / s')
ylabel('activity difference over sample')
subplot(122)
plot(t,c)
xlabel('time / s')
ylabel('mean concentration (kg/kg) in sample')
figure(2);subplot(121) %Ready to zoom on sample activities
%-------------------------end--------------------------------
```

```
%adifanal anlytical solution
beta=input('beta : ');
lambda=input('lambda :');
L=input('L: ');
tau=input('tau : ');

for l=1:length(lambda)
  s=0;
  for b=1:length(beta)
    disp(num2str(beta(b)));
    Ds=2*L*cos(beta(b)*lambda(l))*exp(-beta(b)^2*tau)/ ...
        (beta(b)^2+L^2+L)/cos(beta(b));
    s=s+Ds;
  end
  summa=1-s;
  disp(['lambda=',num2str(lambda(l)),' >>>    C=',num2str(summa),'   last Ds=',num2str(Ds)])
end
```

```
%ADIFTEST
%test of analytical solution and computer simulation
%of activity gradient over sample in SORP4

sorp4sim
clf
figure(4)
sps=input('subplot string: ');
eval(['subplot(',sps,')'])
Dc=delta*Dpair*psat/xi(1)/rho;
plot(t*Dc/h^2,Da,'-')
hold on
alpha=Fmax/As/xi(1)/rho;
L=h*alpha/Dc;
 clear tautau da
 k=0;
maxtau=tend*Dc/h^2;
 for tau=0.3:0.1:maxtau;
  k=k+1;
  tautau(k)=tau;
  da(k)=adiff4(L,tau);
 end
 plot(tautau,da,'--g');
 xlabel('tau')
ylabel('a-diff')
ax=axis;
dx=ax(2)-ax(1);
dy=ax(4)-ax(3);
xx=ax(1)+0.3*dx;
yy=ax(4)-0.5*dy;
text(xx,yy,['h=',num2str(h*1000),' mm'],'FontSize',8)
text(xx,yy-0.05*dy,['rho=',num2str(rho/1000),' g/cm2'],'FontSize',8)
text(xx,yy-0.10*dy,['delta=',num2str(delta)],'FontSize',8)
text(xx,yy-0.15*dy,['sample mass=',num2str(M*1e6),' mg'],'FontSize',8)
text(xx,yy-0.20*dy,['max tau=',num2str(tend/3600),' h'],'FontSize',8)
text(xx,yy-0.25*dy,['L=',num2str(L)],'FontSize',8)
title('solid line = computer simulation, - - - analytical solution')
```

```
hold off
```

```
function bevec=beta(L,n);
%  beta(L,n)
%This matlab function calculates n solutions of the equation
% beta*tan(beta)=L.

global LL
LL=L;
n;
if L<=0.01
  sv0=0.0998;
elseif L<=0.1
  sv0=0.3111;
elseif L<=1
  sv0=0.8603;
elseif L<=10
  sv0=1.4289;
else
  sv0=pi/2;
end
startval=[sv0 pi*(1:(n-1))];
bevec=zeros([1 n]);
for k=1:n
 bevec(k)=fzero('betafunc',startval(k));
end
```

```
function res=betafunc(beta);
global LL

res=beta*tan(beta)-LL;
```

```
function adiff=adiff4(L,tau);
%adiff4
%calculates the difference in activity over a sample in
%the sorption calorimeter SORP4
%
%                    adiff=adiff4(L,tau)
%
%                                        L=ell*alpha/Dc (L<=0.2)
%
%                                        tau=Dc*t/ell^2

if L>0.2
 disp('The equations are not correct for L>0.2');
end
b=beta(L,2);
b1=b(1);
```

```
b2=b(2);
A=2*cos(b2)*exp(-b2^2*tau)/(b2^2+L^2+L);
B=(cos(b1)-1)*exp(-b1^2*tau)/(b1^2+L^2+L)/cos(b1);
adiff=-2*L*(A+B);
%disp(['A=',num2str(A),' B=',num2str(B)])
end
```

```
%adiff
for L=[0.003 0.01:0.01:0.2]
 clear tautau da
 k=0;
 for tau=0.3:0.1:10;
  k=k+1;
  tautau(k)=tau;
  da(k)=adiff4(L,tau);
 end
 plot(tautau,da);
 hold on
 plot(tautau(1),da(1),'o')
end
plot(tautau(1),da(1),'og')
hold off
xlabel('tau')
ylabel('a-diff')
```