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Supporting Material

Kinetic Hysteresis in Collagen Folding

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Appendix

Model 1

abbreviation	meaning
IndVars	independent variables
DepVars	dependent variables
Params	parameters
T	time
TEMP	temperature (K)
F	fraction folded
CD	CD value (ellipticity or mean molar ellipticity)
K	equilibrium constant
K2	rate constant, k_p (s^{-1})
KMIN2	rate constant, k_d (s^{-1})
R	gas constant (8.31 $J \cdot K^{-1} mol^{-1}$)
RATE	rate of heating or cooling ($K \cdot s^{-1}$)
TSTART	temperature at t=0
H	standard enthalpy ($J \cdot mol^{-1}$)
S	standard entropy ($J \cdot K^{-1} mol^{-1}$)
EA	activation energy ($J \cdot mol^{-1}$)
K02	rate constant k_p at 7°C (s^{-1})
CDU	CD value of unfolded state
REFU	reference CD value of unfolded state at 0°C
DEU	slope of linear CD dependence of unfolded state
REFN	reference CD value of folded state at 0°C
DEN	slope of linear CD dependence of folded state

Symbols RATER, TEMPR, TSTARTR, FR, CDR, KR, K2R, KMIN2R have the same meaning as symbols without R as the last letter but refer to the reverse cooling pathway

Symbols in Model 2 are identical to those in Model 1 and in addition,

KA	rate constant, $k_{a,\,app}$ ($M^{-2}s^{-1}$)
KU	rate constant, k_u (s^{-1})
K0A	rate constant $k_{a,\,app}$ at reference temperature (7°C)
K	equilibrium constant (M^{-2})
C0	total peptide concentration c_0 (M)

Symbols in Model 3 are identical to those in Models 1 and 2 and in addition,

FS	fraction of H*
Q	pre-equilibrium constant defined by *Eq.* 14 (M^{-2})
Q7	pre-equilibrium constant at 7°C (M^{-2})
HQ	standard enthalpy of the pre-equilibrium reaction ($J \cdot mol^{-1}$)
SQ	standard entropy of the pre-equilibrium ($J \cdot mol^{-1} K^{-1}$)
FSR	fraction of H* in the reverse cooling pathway

Model 1

// Model 1
IndVars: T
DepVars: TEMP, F, CD, K, K2, KMIN2, TEMPR, FR, CDR, KR, K2R, KMIN2R
Params: H, S, EA, K02, DEU, REFU, DEN, REFN,

F'=3*K2*(1-F)-KMIN2*F
FR'=3*K2R*(1-FR)-KMIN2R*FR

R=8.31
RATE=0.00833333
TSTART=302.96
RATER=-RATE
TSTARTR=343.03

TEMP=TSTART+RATE*T
TEMPR=TSTARTR+RATER*T

TEMP0=280.15

K2=K02*EXP((EA/R)*(1/TEMP0-1/TEMP))
K2R=K02*EXP((EA/R)*(1/TEMP0-1/TEMPR))

KMIN2=K2/K
K=EXP(-(H-TEMP*S)/(R*TEMP))

KMIN2R=K2R/KR
KR=EXP(-(H-TEMPR*S)/(R*TEMPR))

CDU=REFU+DEU*(TEMP-273.15)
CDUR=REFU+DEU*(TEMPR-273.15)

CDN=REFN+DEN*(TEMP-273.15)
CDNR=REFN+DEN*(TEMPR-273.15)

CD=F*(CDN-CDU)+CDU
CDR=FR*(CDNR-CDUR)+CDUR

//INITIAL CONDITIONS
F=1
FR=0
T=0
*****

Model 2

//Model 2

IndVars: T
DepVars: TEMP, CD, CDR, F, TEMPR, FR, K, KA, KU, KAR, KUR, CDN
Params: H, S, EA, K0A, DEU, REFU, DEN, REFN

C0=0.00025
R=8.31
RATE=0.00138889

F'=3*KA*C0^2*(1-F)^3 - KU*F
FR'=3*KAR*C0^2*(1-FR)^3 - KUR*FR

TSTART=278.17
RATER=-RATE
TSTARTR=338.14
TEMP=TSTART+RATE*T
TEMPR=TSTARTR+RATER*T

TEMP0=280.15

KA=K0A*EXP((EA/R)*(1/TEMP0-1/TEMP))
KAR=K0A*EXP((EA/R)*(1/TEMP0-1/TEMPR))

KU=KA/K
K=EXP(-(H-TEMP*S)/(R*TEMP))

KUR=KAR/KR

KR=EXP(-(H-TEMPR*S)/(R*TEMPR))

CDU=REFU+DEU*(TEMP-273.15)
CDUR=REFU+DEU*(TEMPR-273.15)
CDN=REFN+DEN*(TEMP-273.15)
CDNR=REFN+DEN*(TEMPR-273.15)

CD=F*(CDN-CDU)+CDU
CDR=FR*(CDNR-CDUR)+CDUR

//INITIAL CONDITIONS
F=0.999999
FR=0.000001
T=0
*****

Model 3
// Model 3
IndVars: T

DepVars: TEMP, F, FS, CD, K, K2, KMIN2, TEMPR, FR, FSR, CDR, KR, K2R, KMIN2R, Q Params: H, S, HQ, SQ, EA, K02, DEU, REFU, DEN, REFN,

F'=K2*FS-KMIN2*F
FR'=K2R*FSR-KMIN2R*FR

C0=0.000082
R=8.31
RATE=0.002778
TSTART=277.09
RATER=-RATE
TSTARTR=352.44

TEMP=TSTART+RATE*T
TEMPR=TSTARTR+RATER*T

Q=EXP(-(HQ-TEMP*SQ)/(R*TEMP))
QR=EXP(-(HQ-TEMPR*SQ)/(R*TEMPR))
P=1/(3*Q*(C0^2))
B=P*(1-F)
W=(((B^2)/4)+((P^3)/27))^(1/2)
U=((-B/2)+W)^(1/3)
V=-((B/2)+W)^(1/3)
FS= U+V+1-F

PR=1/(3*QR*(C0^2))
BR=PR*(1-FR)
WR=(((BR^2)/4)+((PR^3)/27))^(1/2)
UR=((-BR/2)+WR)^(1/3)
VR=-((BR/2)+WR)^(1/3)
FSR= UR+VR+1-FR

TEMP0=280.15

K2=K02*EXP((EA/R)*(1/TEMP0-1/TEMP))
K2R=K02*EXP((EA/R)*(1/TEMP0-1/TEMPR))

KMIN2=K2*Q/K
K=EXP(-(H-TEMP*S)/(R*TEMP))

KMIN2R=K2R*QR/KR
KR=EXP(-(H-TEMPR*S)/(R*TEMPR))

CDU=REFU+DEU*(TEMP-273.15)
CDUR=REFU+DEU*(TEMPR-273.15)

CDN=REFN+DEN*(TEMP-273.15)
CDNR=REFN+DEN*(TEMPR-273.15)

CD=F*(CDN-CDU)+CDU
CDR=FR*(CDNR-CDUR)+CDUR

//INITIAL CONDITIONS
F=0.999999
FR=0.000001
T=0

For global fitting, the second and the third data set were added for all of variables and parameters shown below as labeled TEMPB, TEMPC, FB, FC etc.
DepVars: TEMP, F, FS, CD, K, K2, KMIN2, TEMPR, FR, FSR, CDR, KR, K2R, KMIN2R, Q
and Params: DEU, REFU, DEN, REFN