APPENDIX C: PROGRAMS

C.1 Application of Existing UNIFAC Dortmund Parameters from the DDBST

Sample programs for the application of existing parameters from the DDBST are shown in this section, where the programs used are for the system ethanol (1) + water (2) + glycerol (3).

C.1.1 Optimization Program

The optimization program for ethanol (1) + water (2) + glycerol (3) is presented as follows with a file name *udod25*.

```
%Define number of components, subgroups
and data

comp=6;
subgroup=9;
data=36;

%Define initial guesses for the
predicted bubble points, store in 'g'

Texp=[370.37
      359.77
      362
      368.7
      380.87
      372.52
      356.67
      367.73
      363.85
      356.89
      356.05
      356.35
      355.77
      358.4
      359.67
      363.75
      354.95
      365.87
      362
      358.75
      353.84
      353.93
      353.92
      356.72
      355.07
      354.79
      358.9
      354.82
      354.11
      356.99
      352.84
      355.23
      353.8
      355.32
      353.61
      355.53];

g=zeros(data,1);

for n=1:data
    g(n)=Texp(n);
end

%Define lower and upper bounds for
predicted bubble points

A=[];
d=[];
Aeq=[];
beq=[];

lb=zeros(data,1);

for n=1:data
    lb(n)=350.15;
end

ub=zeros(data,1);

for n=1:data
    ub(n)=473.15;
end

%Optimization Process, solve for
predicted bubble points, store in 'p'

options=optimset('MaxFunEvals',120000);
options=optimset(options,'MaxIter',10000
0);
options=optimset(options,'disp','iter','
LargeScale','off','TolFun',.0000000001);
p=fmincon(@udod23,g,A,d,Aeq,beq,lb,ub,@u
dod24,options)
```

C.1.2 Objective Function Subprogram

The objective function subprogram for ethanol (1) + water (2) + glycerol (3) is presented as follows with a file name *udod23*.

```
function f=udod23(g)

%Define number of data

data=36;

%Define experimental bubble points

Texp=[370.37
      359.77
      362
      368.7
      380.87
      372.52
      356.67
      367.73
      363.85
      356.89
      356.05
      356.35
      355.77
      358.4
      359.67
      363.75
      354.95
      365.87
      362
      358.75
      353.84
      353.93
      353.92
      356.72
      355.07
      354.79
      358.9
      354.82
      354.11
      356.99
      352.84
      355.23
      353.8
      355.32
      353.61
      355.53];

%Define predicted bubble points as 'g'

Ttheo=zeros(data,1);

for n=1:data
    Ttheo(n)=g(n);
end

%Define objective function

f=0;
for n=1:data
    f=f+(Texp(n)-Ttheo(n))^2;
end
```

C.1.3 UNIFAC Dortmund Model Subprogram

The UNIFAC Dortmund model subprogram for ethanol (1) + water (2) + glycerol (3) is presented as follows with a file name *udod24*.

```
function [cineq,ceq]=udod24(g)

%Define number of components, subgroups and data

comp=6;
subgroup=9;
data=36;

%Define experimental data
P=101325;
x=[0.065    0.676   0.259 0 0 0
   0.092    0.842   0.066 0 0 0
   0.097    0.747   0.156 0 0 0
   0.1      0.553   0.347 0 0 0
   0.107    0.305   0.588 0 0 0
   0.175    0.242   0.583 0 0 0
```

```
   0.19     0.756   0.054 0 0 0
   0.197    0.296   0.507 0 0 0
   0.198    0.424   0.378 0 0 0
   0.209    0.681   0.11  0 0 0
   0.245    0.71    0.045 0 0 0
   0.258    0.706   0.036 0 0 0
   0.286    0.626   0.088 0 0 0
   0.302    0.42    0.278 0 0 0
   0.307    0.325   0.368 0 0 0
   0.308    0.196   0.496 0 0 0
   0.344    0.632   0.024 0 0 0
   0.365    0.076   0.559 0 0 0
   0.411    0.101   0.488 0 0 0
   0.416    0.205   0.379 0 0 0
   0.43     0.533   0.037 0 0 0
   0.465    0.425   0.11  0 0 0
   0.47     0.478   0.052 0 0 0
   0.491    0.201   0.308 0 0 0
   0.497    0.375   0.128 0 0 0
   0.504    0.333   0.163 0 0 0
   0.57     0.043   0.387 0 0 0
   0.583    0.272   0.145 0 0 0
   0.584    0.315   0.101 0 0 0
   0.608    0.092   0.3   0 0 0
   0.671    0.276   0.053 0 0 0
   0.7      0.122   0.178 0 0 0
   0.7      0.204   0.096 0 0 0
   0.777    0.036   0.187 0 0 0
   0.811    0.102   0.087 0 0 0
   0.898    0.037   0.065 0 0 0];

%Define Rk, Qk, and vk values

R=[0.6325;0.6325;0.6325;1.2302;1.063;1.7334;0.9861;3;3];
Q=[1.0608;0.7081;0.3554;0.8927;0.8663;2.4561;0.9917;3;3];
v=[1    0   0   0   0   0
    1   0   2   0   0   0
    0   0   1   0   0   0
    1   0   2   0   0   0
    0   0   1   0   0   0
    0   1   0   0   0   0
    0   0   0   1   0   0
    0   0   0   0   1   0
    0   0   0   0   0   1];

r=zeros(comp,1);
q=zeros(comp,1);

for i=1:comp
    for k=1:subgroup
        r(i)=r(i)+R(k)*v(k,i);
        q(i)=q(i)+Q(k)*v(k,i);
    end
end

%Define binary interaction parameters

a=[0    0   0   2777    2777    1391.3  6731.4  6767.4  -2071.6
   0    0   0   2777    2777    1391.3  6731.4  6767.4  -2071.6
   0    0   0   2777    2777    1391.3  6731.4  6767.4  -2071.6
   1606 1606    1606    0   0   -801.9  4286.2  -7007.6 -5941.1
   1606 1606    1606    0   0   -801.9  4286.2  -7007.6 -5941.1
   -17.253  -17.253 -17.253 1460    1460    0   5.3069  -1970.2 -5616.8
   -7424.5  -7424.5 -7424.5 4950.2  4950.2  -144.82 0   -2425.8 -6110.8
   -1899    -1899   -1899   -2974.7 -2974.7 -552.42 23275   0   0
```

```
   12803    12803   12803   399.74  399.74  -481.55 18.581  0   0];
b=[0    0   0   -4.674  -4.674  -3.6156 47  49.151  0.228
   0    0   0   -4.674  -4.674  -3.6156 47  49.151  0.228
   0    0   0   -4.674  -4.674  -3.6156 47  49.151  0.228
   -4.746   -4.746  -4.746  0   0   3.824   -62.547 14.053  0.0032
   -4.746   -4.746  -4.746  0   0   3.824   -62.547 14.053  0.0032
   0.8389   0.8389  0.8389  -8.673  -8.673  0   0.4377  1.2864  0.4801
   20.728   20.728  20.728  -15.522 -15.522 -0.0174 0   0.0221  0
   72.291   72.291  72.291  8.1759  8.1759  -0.0097 2.224   0   0
   5.1318   5.1318  5.1318  0.0053  0.0053  -0.0051 0   0   0];


c=[0    0   0   0.001551    0.001551    0.001144    0   0   0
   0    0   0   0.001551    0.001551    0.001144    0   0   0
   0    0   0   0.001551    0.001551    0.001144    0   0   0
   0.0009181    0.0009181   0.0009181   0   0   -0.007514   0   0   0
   0.0009181    0.0009181   0.0009181   0   0   -0.007514   0   0   0
   0.0009021    0.0009021   0.0009021   0.01641 0.01641 0   0   0   0
   0    0   0   0   0   0   0   0   0
   0    0   0   0   0   0   0   0   0
   0    0   0   0   0   0   0   0   0];

%Define predicted bubble points as 'g'

Ttheo=zeros(data,1);

for n=1:data
    Ttheo(n)=g(n);
end

%Calculation of activity coefficients using UNIFAC Dortmund model

e=zeros(subgroup,comp);

for i=1:comp
    for k=1:subgroup
        e(k,i)=v(k,i)*Q(k)/q(i);
    end
end

tau=zeros(subgroup,subgroup,data);

for n=1:data
    for k=1:subgroup
        for m=1:subgroup
            tau(m,k,n)=exp(-(a(m,k)+b(m,k)*Ttheo(n)+c(m,k)*Ttheo(n)^2)/Ttheo(n));
        end
    end
end

B=zeros(subgroup,comp,data);

for n=1:data
    for i=1:comp
        for k=1:subgroup
            for m=1:subgroup
                B(k,i,n)=B(k,i,n)+e(m,i)*tau(m,k,n);
            end
        end
    end
end

numtheta=zeros(subgroup,data);
denomtheta=zeros(subgroup,data);
theta=zeros(subgroup,data);
```

```
for n=1:data
    for k=1:subgroup
        for i=1:comp
            numtheta(k,n)=numtheta(k,n)+x(n,i)*q(i)*e(k,i);
            denomtheta(k,n)=denomtheta(k,n)+x(n,i)*q(i);
            theta(k,n)=numtheta(k,n)/denomtheta(k,n);
        end
    end
end


s=zeros(subgroup,data);


for n=1:data
    for k=1:subgroup
        for m=1:subgroup
            s(k,n)=s(k,n)+theta(m,n)*tau(m,k,n);
        end
    end
end

sum=zeros(comp,data);

for n=1:data
    for i=1:comp
        for k=1:subgroup
            sum(i,n)=sum(i,n)+theta(k,n)*B(k,i,n)/s(k,n)-e(k,i)*log(B(k,i,n)/s(k,n));
        end
    end
end

denomJ=zeros(comp,data);
denomJmod=zeros(comp,data);
denomL=zeros(comp,data);
J=zeros(comp,data);
Jmod=zeros(comp,data);
L=zeros(comp,data);

for n=1:data
    for i=1:comp
        for j=1:comp
            denomJ(i,n)=denomJ(i,n)+r(j)*x(n,j);
            J(i,n)=r(i)/denomJ(i,n);
            denomJmod(i,n)=denomJmod(i,n)+r(j)^0.75*x(n,j);
            Jmod(i,n)=r(i)^0.75/denomJmod(i,n);
            denomL(i,n)=denomL(i,n)+q(j)*x(n,j);
            L(i,n)=q(i)/denomL(i,n);
        end
    end
end

lngammaR=zeros(comp,data);
lngammaC=zeros(comp,data);
gammatheo=zeros(comp,data);

for n=1:data
    for i=1:comp
        lngammaR(i,n)=q(i)*(1-sum(i,n));
        lngammaC(i,n)=1-Jmod(i,n)+log(Jmod(i,n))-5*q(i)*(1-
J(i,n)/L(i,n)+log(J(i,n)/L(i,n)));
        gammatheo(i,n)=exp(lngammaR(i,n)+lngammaC(i,n));
    end
end
```

```
%Calculation of vapor mole fraction values

Psattheo=zeros(3,data);

for m=1:data
    Psattheo(1,m)=100000*exp(12.2917-3803.98/(Ttheo(m)-41.68));
    Psattheo(2,m)=100000*exp(11.6834-3816.44/(Ttheo(m)-46.13));
    Psattheo(3,m)=0;
end


ytheo=zeros(3,data);



for m=1:data
    for i=1:3
        ytheo(i,m)=gammatheo(i,m)*x(m,i)*Psattheo(i,m)/P;
    end
end

%Calculate summation of y, constraint as equal to 1

cineq=[];
ceq=zeros(1,data);

for m=1:data
    ceq(m)=ytheo(1,m)+ytheo(2,m)+ytheo(3,m)-1;
end
```

C.2 Estimation of New Parameters for the CNH_2 – OH Interaction

In this section, sample programs for the estimation of new parameters for CNH_2 – OH interaction are shown, where the programs used are for the ethanol (1) + water (2) + TRIS (10) system.

C.2.1 Optimization Program

The optimization subprogram for ethanol (1) + water (2) + TRIS (10) is presented as follows with a file name *udod210*.

```
%Define number of components, subgroups
and data

comp=3;
subgroup=6;
data=36;

%Define experimental bubble points

Texp=[365.15
      360.15
      358.65
      356.15
      354.65
      353.65
      352.15
      352.15
      351.65
      365.15
      359.15
      356.65
      354.65
      353.65
      352.15
      351.65
      351.65
      351.65
      365.15
      359.15
      356.15
```

```
      355.15
      354.15
      353.15
      352.65
      352.15
      351.65
      364.65
      359.15
      356.15
      354.15
      353.65
      352.65
      352.65
      351.65
      351.65];

%Set experimental bubble points as
initial guesses

Ttheoig=zeros(data,1);

for n=1:data
    Ttheoig(n)=Texp(n);
end

%Set some parameters as initial guesses

a=[0 0 2777 1391.3 -164.04 994.18;
   0 0 2777 1391.3 -164.04 994.18;
   1606 1606 0 -801.9 -923.7 -290.93;
   -17.253 -17.253 1460 0 798.5
1952.444;
   326.04 326.04 -75.63 -980.6 0
2000.373;
   -3382.44 -3382.44 -3202.57 -767.738 -
4058.09 0];
b=[0 0 -4.674 -3.6156 4.9683 0.5935;
   0 0 -4.674 -3.6156 4.9683 0.5935;
   -4.746 -4.746 0 3.824 2.468 18.862;
   0.8389 0.8389 -8.673 0 -5.869 -
12.974;
   -2.6348 -2.6348 -0.1511 3.671 0
8.365;
   17.27 17.27 8.402 5.371 -19.998 0];
c=[0 0 0.001551 0.001144 -0.010252 0;
   0 0 0.001551 0.001144 -0.010252 0;
   0.0009181 0.0009181 0 -0.007514 -
0.045757 0;
   0.0009021 0.0009021 0.01641 0 0.01032
0;
   0.0033576 0.0033576 0.0347487 -
0.005908 0 0;
   0 0 0 0 0 0];

a(6,1)=par2(1);
a(6,2)=a(6,1);
a(6,3)=par2(2);
a(6,4)=par2(3);

a(1,6)=par2(4);
a(2,6)=a(1,6);
a(3,6)=par2(5);
a(4,6)=par2(6);

b(6,1)=par2(7);
b(6,2)=b(6,1);
b(6,3)=par2(8);
b(6,4)=par2(9);

b(1,6)=par2(10);
b(2,6)=b(1,6);
b(3,6)=par2(11);
b(4,6)=par2(12);

c(5,3)=par3(1);
c(3,5)=par3(2);

%Store initial guesses in 'g'

g=zeros(data+2,1);

for n=1:data
    g(n)=Ttheoig(n);
end

g(data+1)=c(5,3);
g(data+2)=c(3,5);

%Define lower and upper bounds for
unknowns

A=[];
d=[];
Aeq=[];
beq=[];

lb=zeros(data+2,1);

for n=1:data
    lb(n)=345;
end

for n=data+1:data+2
    lb(n)=-0.08;
end

ub=zeros(data+2,1);

for n=1:data
    ub(n)=380;
end

for n=data+1:data+2
    ub(n)=0.08;
end

%Optimization Process, solve for
predicted bubble points and parameters,
store in 'p'

options=optimset('MaxFunEvals',150000);
options=optimset(options,'MaxIter',15000
0);
options=optimset(options,'disp','iter','
LargeScale','off','TolFun',0);
p=fmincon(@udod208,g,A,d,Aeq,beq,lb,ub,@
udod209,options);
```

C.2.2 Objective Function Subprogram

The objective function subprogram for ethanol (1) + water (2) + TRIS (10) is presented as follows with a file name *udod208*.

```
function f=udod208(g)

%Define number of components, subgroups
and data

comp=3;
subgroup=6;
data=36;

%Define experimental data

P=101325;
x=[0.0313   0.9668  0.0018865
   0.0788   0.9191  0.0020196
   0.112    0.8859  0.0021124
   0.2187   0.7789  0.0024112
   0.3378   0.6595  0.0027448
   0.4395   0.5575  0.0030297
   0.6204   0.3761  0.0035365
   0.6885   0.3077  0.0037273
   0.833    0.1628  0.0041321
   0.0336   0.9626  0.0037788
   0.1003   0.8956  0.0041518
   0.2043   0.7909  0.0047336
   0.3445   0.65    0.0055174
   0.453    0.5409  0.0061242
   0.6182   0.3747  0.007048
   0.7735   0.2186  0.0079165
   0.8423   0.1493  0.0083013
   0.8785   0.113   0.0085033
   0.0341   0.9602  0.0056625
   0.1013   0.8925  0.0062248
   0.1998   0.7932  0.0070497
   0.2835   0.7088  0.0077505
   0.4065   0.5847  0.0087804
   0.4952   0.4952  0.0095234
   0.5474   0.4426  0.0099601
   0.6969   0.2919  0.011212
   0.7555   0.2328  0.011702
   0.0377   0.9547  0.0075767
   0.1017   0.8901  0.0082892
   0.1973   0.7933  0.0093555
   0.374    0.6147  0.011324
   0.5008   0.4864  0.012738
   0.6564   0.3292  0.014471
   0.7675   0.2168  0.015709
   0.8228   0.1608  0.016326
   0.8476   0.1358  0.016602];

yexp=[0.2167    0.7833
      0.3783    0.6217
      0.4632    0.5368
      0.569     0.431
      0.6036    0.3964
      0.6433    0.3567
      0.7048    0.2952
      0.7338    0.2662
      0.8619    0.1381
      0.2217    0.7783
      0.4632    0.5368
      0.569     0.431
      0.6433    0.3567
      0.6911    0.3089
      0.749     0.251
      0.8365    0.1635
      0.886     0.114
      0.9101    0.0899
      0.246     0.754
      0.4779    0.5221
      0.5773    0.4227
      0.6327    0.3673
      0.6782    0.3218
      0.719     0.281
      0.749     0.251
      0.8231    0.1769
      0.8619    0.1381
      0.2913    0.7087
      0.4926    0.5074
      0.6036    0.3964
      0.6782    0.3218
      0.7644    0.2356
      0.8365    0.1635
      0.886     0.114
      0.9226    0.0774
      0.9362    0.0638];

%Define Rk, Qk, and vk values

R=[0.6325;0.6325;1.2302;1.7334;1.6607;0.
9861];
Q=[1.0608;0.7081;0.8927;2.4561;0.985;0.9
917];
v=[1 0 0 0;
   1 0 3 0;
   1 0 3 0;
   0 1 0 0;
   0 0 1 0;
   0 0 0 1];

r=zeros(comp,1);
q=zeros(comp,1);

for i=1:comp
    for k=1:subgroup
        r(i)=r(i)+R(k)*v(k,i);
        q(i)=q(i)+Q(k)*v(k,i);
    end
end

%Define binary interaction parameters

a=[0 0 2777 1391.3 -164.04 994.18;
   0 0 2777 1391.3 -164.04 994.18;
   1606 1606 0 -801.9 -923.7 -290.93;
```

```
   -17.253 -17.253 1460 0 798.5
1952.444;
   326.04 326.04 -75.63 -980.6 0
2000.373;
   -3382.44 -3382.44 -3202.57 -767.738 -
4058.09 0];
b=[0 0 -4.674 -3.6156 4.9683 0.5935;
   0 0 -4.674 -3.6156 4.9683 0.5935;
   -4.746 -4.746 0 3.824 2.468 18.862;
   0.8389 0.8389 -8.673 0 -5.869 -
12.974;
   -2.6348 -2.6348 -0.1511 3.671 0
8.365;
   17.27 17.27 8.402 5.371 -19.998 0];
c=[0 0 0.001551 0.001144 -0.010252 0;
   0 0 0.001551 0.001144 -0.010252 0;
   0.0009181 0.0009181 0 -0.007514 -
0.045757 0;
   0.0009021 0.0009021 0.01641 0 0.01032
0;
   0.0033576 0.0033576 0.0347487 -
0.005908 0 0;
   0 0 0 0 0 0];

%Define unknowns as 'g'

Ttheo=zeros(data,1);

for n=1:data
    Ttheo(n)=g(n);
end

c(5,3)=g(data+1);
c(3,5)=g(data+2);

%Calculation of activity coefficients
using UNIFAC Dortmund model

e=zeros(subgroup,comp);

for i=1:comp
    for k=1:subgroup
        e(k,i)=v(k,i)*Q(k)/q(i);
    end
end

%Parameters Involving NaCl and KCl

par=[-7424.503033
4950.20659
-144.8225851
-1898.999987
-2974.697256
-552.4191876
23274.9996
12802.99989
399.7443569
-481.553246
18.58099987
6731.399951
4286.19997
5.306899964
6767.399951
-7007.599079
-1970.197925
-2425.8029
-2071.599999
-5941.097387
-5616.80291
-6110.799563
19.32297127
-13.0271048
-0.294090924
72.19761192
9.231719
0.325269273
2.222623898
5.128617894
1.481264641
0.372763723
4.03E-18
46.96271044
-62.48354716
0.437429301
49.11094333
14.41223902
2.039060088
-1.093824478
0.222932659
0.674638133
1.368392024
-1.555090141];

par2=zeros(12,1);

par2(1)=par(1);
par2(2)=par(2);
par2(3)=par(3);
par2(4)=par(12);
par2(5)=par(13);
par2(6)=par(14);
par2(7)=par(23);
par2(8)=par(24);
par2(9)=par(25);
par2(10)=par(34);
par2(11)=par(35);
par2(12)=par(36);

a(6,1)=par2(1);
a(6,2)=a(6,1);
a(6,3)=par2(2);
a(6,4)=par2(3);

a(1,6)=par2(4);
a(2,6)=a(1,6);
a(3,6)=par2(5);
a(4,6)=par2(6);

b(6,1)=par2(7);
b(6,2)=b(6,1);
b(6,3)=par2(8);
b(6,4)=par2(9);

b(1,6)=par2(10);
b(2,6)=b(1,6);
b(3,6)=par2(11);
b(4,6)=par2(12);

tau=zeros(subgroup,subgroup,data);
```

```
for n=1:data
    for k=1:subgroup
        for m=1:subgroup
            tau(m,k,n)=exp(-
(a(m,k)+b(m,k)*Ttheo(n)+c(m,k)*Ttheo(n)^
2)/Ttheo(n));
        end
    end
end

B=zeros(subgroup,comp,data);

for n=1:data
    for i=1:comp
        for k=1:subgroup
            for m=1:subgroup

B(k,i,n)=B(k,i,n)+e(m,i)*tau(m,k,n);
            end
        end
    end
end

numtheta=zeros(subgroup,data);
denomtheta=zeros(subgroup,data);
theta=zeros(subgroup,data);

for n=1:data
    for k=1:subgroup
        for i=1:comp

numtheta(k,n)=numtheta(k,n)+x(n,i)*q(i)*
e(k,i);

denomtheta(k,n)=denomtheta(k,n)+x(n,i)*q
(i);

theta(k,n)=numtheta(k,n)/denomtheta(k,n)
;
        end
    end
end

s=zeros(subgroup,data);

for n=1:data
    for k=1:subgroup
        for m=1:subgroup

s(k,n)=s(k,n)+theta(m,n)*tau(m,k,n);
        end
    end
end

sum=zeros(comp,data);

for n=1:data
    for i=1:comp
        for k=1:subgroup

sum(i,n)=sum(i,n)+theta(k,n)*B(k,i,n)/s(
k,n)-e(k,i)*log(B(k,i,n)/s(k,n));
        end
    end
end

denomJ=zeros(comp,data);
denomJmod=zeros(comp,data);
denomL=zeros(comp,data);
J=zeros(comp,data);
Jmod=zeros(comp,data);
L=zeros(comp,data);

for n=1:data
    for i=1:comp
        for j=1:comp

denomJ(i,n)=denomJ(i,n)+r(j)*x(n,j);
            J(i,n)=r(i)/denomJ(i,n);

denomJmod(i,n)=denomJmod(i,n)+r(j)^0.75*
x(n,j);

Jmod(i,n)=r(i)^0.75/denomJmod(i,n);

denomL(i,n)=denomL(i,n)+q(j)*x(n,j);
            L(i,n)=q(i)/denomL(i,n);
        end
    end
end

lngammaR=zeros(comp,data);
lngammaC=zeros(comp,data);
gammatheo=zeros(comp,data);

for n=1:data
    for i=1:comp
        lngammaR(i,n)=q(i)*(1-sum(i,n));
        lngammaC(i,n)=1-
Jmod(i,n)+log(Jmod(i,n))-5*q(i)*(1-
J(i,n)/L(i,n)+log(J(i,n)/L(i,n)));

gammatheo(i,n)=exp(lngammaR(i,n)+lngamma
C(i,n));
    end
end

%Calculation of vapor mole fraction
values

Psattheo=zeros(2,data);

for m=1:data
    Psattheo(1,m)=100000*exp(12.2917-
3803.98/(Ttheo(m)-41.68));
    Psattheo(2,m)=100000*exp(11.6834-
3816.44/(Ttheo(m)-46.13));
end

ytheo=zeros(data,2);

for m=1:data
    for j=1:2

ytheo(m,j)=gammatheo(j,m)*x(m,j)*Psatthe
o(j,m)/P;
    end
end
```

```
%Define objective function

f=0;
for n=1:data
    for j=1:2
        f=f+(yexp(n,j)-
ytheo(n,j))^2/(yexp(n,j))^2;
    end
end
```

C.2.3 UNIFAC Dortmund Model Subprogram

The UNIFAC Dortmund model subprogram for ethanol (1) + water (2) + TRIS (10) is presented as follows with a file name *udod209*.

```
function [cineq,ceq]=udod209(g)

%Define number of components, subgroups
and data

comp=3;
subgroup=6;
data=36;

%Define experimental data

P=101325;
x=[0.0313   0.9668  0.0018865
   0.0788   0.9191  0.0020196
   0.112    0.8859  0.0021124
   0.2187   0.7789  0.0024112
   0.3378   0.6595  0.0027448
   0.4395   0.5575  0.0030297
   0.6204   0.3761  0.0035365
   0.6885   0.3077  0.0037273
   0.833    0.1628  0.0041321
   0.0336   0.9626  0.0037788
   0.1003   0.8956  0.0041518
   0.2043   0.7909  0.0047336
   0.3445   0.65    0.0055174
   0.453    0.5409  0.0061242
   0.6182   0.3747  0.007048
   0.7735   0.2186  0.0079165
   0.8423   0.1493  0.0083013
   0.8785   0.113   0.0085033
   0.0341   0.9602  0.0056625
   0.1013   0.8925  0.0062248
   0.1998   0.7932  0.0070497
   0.2835   0.7088  0.0077505
   0.4065   0.5847  0.0087804
   0.4952   0.4952  0.0095234
   0.5474   0.4426  0.0099601
   0.6969   0.2919  0.011212
   0.7555   0.2328  0.011702
   0.0377   0.9547  0.0075767
   0.1017   0.8901  0.0082892
   0.1973   0.7933  0.0093555
   0.374    0.6147  0.011324
   0.5008   0.4864  0.012738
   0.6564   0.3292  0.014471
   0.7675   0.2168  0.015709
   0.8228   0.1608  0.016326
   0.8476   0.1358  0.016602];

%Define Rk, Qk, and vk values

R=[0.6325;0.6325;1.2302;1.7334;1.6607;0.
9861];
Q=[1.0608;0.7081;0.8927;2.4561;0.985;0.9
917];
v=[1 0 0 0;
   1 0 3 0;
   1 0 3 0;
   0 1 0 0;
   0 0 1 0;
   0 0 0 1];

r=zeros(comp,1);
q=zeros(comp,1);

for i=1:comp
    for k=1:subgroup
        r(i)=r(i)+R(k)*v(k,i);
        q(i)=q(i)+Q(k)*v(k,i);
    end
end

%Define binary interaction parameters

a=[0 0 2777 1391.3 -164.04 994.18;
   0 0 2777 1391.3 -164.04 994.18;
   1606 1606 0 -801.9 -923.7 -290.93;
   -17.253 -17.253 1460 0 798.5
1952.444;
   326.04 326.04 -75.63 -980.6 0
2000.373;
   -3382.44 -3382.44 -3202.57 -767.738 -
4058.09 0];
b=[0 0 -4.674 -3.6156 4.9683 0.5935;
   0 0 -4.674 -3.6156 4.9683 0.5935;
   -4.746 -4.746 0 3.824 2.468 18.862;
   0.8389 0.8389 -8.673 0 -5.869 -
12.974;
   -2.6348 -2.6348 -0.1511 3.671 0
8.365;
   17.27 17.27 8.402 5.371 -19.998 0];
c=[0 0 0.001551 0.001144 -0.010252 0;
   0 0 0.001551 0.001144 -0.010252 0;
   0.0009181 0.0009181 0 -0.007514 -
0.045757 0;
   0.0009021 0.0009021 0.01641 0 0.01032
0;
   0.0033576 0.0033576 0.0347487 -
0.005908 0 0;
   0 0 0 0 0 0];
```

```
%Define unknowns as 'g'

Ttheo=zeros(data,1);

for n=1:data
    Ttheo(n)=g(n);
end

c(5,3)=g(data+1);
c(3,5)=g(data+2);

%Calculation of activity coefficients
using UNIFAC Dortmund model

e=zeros(subgroup,comp);

for i=1:comp
    for k=1:subgroup
        e(k,i)=v(k,i)*Q(k)/q(i);
    end
end

%Parameters Involving NaCl and KCl

par=[-7424.503033
4950.20659
-144.8225851
-1898.999987
-2974.697256
-552.4191876
23274.9996
12802.99989
399.7443569
-481.553246
18.58099987
6731.399951
4286.19997
5.306899964
6767.399951
-7007.599079
-1970.197925
-2425.8029
-2071.599999
-5941.097387
-5616.80291
-6110.799563
19.32297127
-13.0271048
-0.294090924
72.19761192
9.231719
0.325269273
2.222623898
5.128617894
1.481264641
0.372763723
4.03E-18
46.96271044
-62.48354716
0.437429301
49.11094333
14.41223902
2.039060088
-1.093824478
0.222932659
0.674638133
1.368392024
-1.555090141];

par2=zeros(12,1);

par2(1)=par(1);
par2(2)=par(2);
par2(3)=par(3);
par2(4)=par(12);
par2(5)=par(13);
par2(6)=par(14);
par2(7)=par(23);
par2(8)=par(24);
par2(9)=par(25);
par2(10)=par(34);
par2(11)=par(35);
par2(12)=par(36);

a(6,1)=par2(1);
a(6,2)=a(6,1);
a(6,3)=par2(2);
a(6,4)=par2(3);

a(1,6)=par2(4);
a(2,6)=a(1,6);
a(3,6)=par2(5);
a(4,6)=par2(6);

b(6,1)=par2(7);
b(6,2)=b(6,1);
b(6,3)=par2(8);
b(6,4)=par2(9);

b(1,6)=par2(10);
b(2,6)=b(1,6);
b(3,6)=par2(11);
b(4,6)=par2(12);

tau=zeros(subgroup,subgroup,data);

for n=1:data
    for k=1:subgroup
        for m=1:subgroup
            tau(m,k,n)=exp(-
(a(m,k)+b(m,k)*Ttheo(n)+c(m,k)*Ttheo(n)^
2)/Ttheo(n));
        end
    end
end

B=zeros(subgroup,comp,data);

for n=1:data
    for i=1:comp
        for k=1:subgroup
            for m=1:subgroup

B(k,i,n)=B(k,i,n)+e(m,i)*tau(m,k,n);
            end
        end
    end
end
```

```
numtheta=zeros(subgroup,data);
denomtheta=zeros(subgroup,data);
theta=zeros(subgroup,data);

for n=1:data
    for k=1:subgroup
        for i=1:comp

numtheta(k,n)=numtheta(k,n)+x(n,i)*q(i)*
e(k,i);

denomtheta(k,n)=denomtheta(k,n)+x(n,i)*q
(i);

theta(k,n)=numtheta(k,n)/denomtheta(k,n)
;
        end
    end
end

s=zeros(subgroup,data);

for n=1:data
    for k=1:subgroup
        for m=1:subgroup

s(k,n)=s(k,n)+theta(m,n)*tau(m,k,n);
        end
    end
end

sum=zeros(comp,data);

for n=1:data
    for i=1:comp
        for k=1:subgroup

sum(i,n)=sum(i,n)+theta(k,n)*B(k,i,n)/s(
k,n)-e(k,i)*log(B(k,i,n)/s(k,n));
        end
    end
end

denomJ=zeros(comp,data);
denomJmod=zeros(comp,data);
denomL=zeros(comp,data);
J=zeros(comp,data);
Jmod=zeros(comp,data);
L=zeros(comp,data);

for n=1:data
    for i=1:comp
        for j=1:comp

denomJ(i,n)=denomJ(i,n)+r(j)*x(n,j);
            J(i,n)=r(i)/denomJ(i,n);

denomJmod(i,n)=denomJmod(i,n)+r(j)^0.75*
x(n,j);

Jmod(i,n)=r(i)^0.75/denomJmod(i,n);

denomL(i,n)=denomL(i,n)+q(j)*x(n,j);
            L(i,n)=q(i)/denomL(i,n);
        end
    end
end

lngammaR=zeros(comp,data);
lngammaC=zeros(comp,data);
gammatheo=zeros(comp,data);

for n=1:data
    for i=1:comp
        lngammaR(i,n)=q(i)*(1-sum(i,n));
        lngammaC(i,n)=1-
Jmod(i,n)+log(Jmod(i,n))-5*q(i)*(1-
J(i,n)/L(i,n)+log(J(i,n)/L(i,n)));

gammatheo(i,n)=exp(lngammaR(i,n)+lngamma
C(i,n));
    end
end

%Calculation of vapor mole fraction
values

Psattheo=zeros(2,data);

for m=1:data
    Psattheo(1,m)=100000*exp(12.2917-
3803.98/(Ttheo(m)-41.68));
    Psattheo(2,m)=100000*exp(11.6834-
3816.44/(Ttheo(m)-46.13));
end

ytheo=zeros(data,2);

for m=1:data
    for j=1:2

ytheo(m,j)=gammatheo(j,m)*x(m,j)*Psatthe
o(j,m)/P;
    end
end

cineq=[];
ceq=zeros(1,data);

for m=1:data
    ceq(m)=ytheo(m,1)+ytheo(m,2)-1;
end
```

C.2.4 Randomization of Initial Guesses for Parameters

The randomization of the initial guesses for the ethanol (1) + water (2) + TRIS (10) is presented as follows with a file name *udod174*.

```
par3=zeros(2,1);

for i=1:2
    par3(i)=-0.05+0.1*rand;
end
```

C.3 Revision of New Parameters for Interactions with NaCl and KCl

In this section, sample programs for the revision of new parameters for interactions with NaCl and KCl are shown:

C.3.1 Optimization Program

The optimization program for the revision of new parameters for interactions with NaCl and KCl is presented as follows with a file name *udod106*.

```
%Define number of components, subgroups
and data

comp=6;
subgroup=8;
data=85;
datap=data+44;
Tdev=3;

%Define experimental bubble points

Texp1=[352.95
       353.55
       353.55
       353.95
       354.85
       354.95
       355.75
       356.85
       358.05
       353.95
       354.65
       354.75
       354.85
       356.15
       356.45
       357.75
       360.15
       360.35];

Texp2=[354.05
       354.25
       354.35
       354.65
       355.05
       355.65
       355.75
       355.75
       356.15
       356.25
       356.65
       357.25
       357.55
       357.65
       358.45
       358.75
       360.15
       353.05
       353.55
       353.75
       354.75
       354.75
       355.45
       355.65
       355.75
       355.85
       355.95
       355.95
       356.05
       356.15
       356.15
       356.25
       356.35
       356.35
       356.55
       356.65
       356.65
       356.85
```

```
      356.95
      357.05
      357.15
      357.15
      357.15
      357.25
      357.45
      357.75
      357.75
      357.85
      358.25
      358.45
      358.65
      358.85
      358.95
      359.15
      359.25
      359.55
      359.55
      359.65
      360.35
      360.65
      360.85
      361.95
      363.35
      363.75
      364.15
      364.55
      367.55];

Texp=zeros(data,1);

for i=1:18
    Texp(i)=Texp1(i);
end

for i=19:data
    Texp(i)=Texp2(i-18);
end

%Set experimental bubble points as
initial guesses

Ttheoig=zeros(data,1);

for n=1:data
    Ttheoig(n)=Texp(n)+Tdev;
end

%Set some parameters as initial guesses

a=[0 0 0 2777 1391.3 6731.4 6767.4 -
2071.6;
   0 0 0 2777 1391.3 6731.4 6767.4 -
2071.6;
   0 0 0 2777 1391.3 6731.4 6767.4 -
2071.6;
   1606 1606 1606 0 -801.9 4286.2 -
7007.6 -5941.1;
   -17.253 -17.253 -17.253 1460 0 5.3069
-1970.2 -5616.8;
   -7424.5 -7424.5 -7424.5 4950.2 -
144.82 0 -2425.8 -6110.8;
   -1899 -1899 -1899 -2974.7 -552.42
23275 0 1000;
   12803 12803 12803 399.74 -481.55
18.581 1000 0];
b=[0 0 0 -4.674 -3.6156 47 49.151 0.228;
   0 0 0 -4.674 -3.6156 47 49.151 0.228;
   0 0 0 -4.674 -3.6156 47 49.151 0.228;
   -4.746 -4.746 -4.746 0 3.824 -62.547
14.053 0.0032;
   0.8389 0.8389 0.8389 -8.673 0 0.4377
1.2864 0.4801;
   20.728 20.728 20.728 -15.522 -0.0174
0 0.0221 0;
   72.291 72.291 72.291 8.1759 -0.0097
2.224 0 1;
   5.1318 5.1318 5.1318 0.0053 -0.0051 0
1 0];

%Store initial guesses in 'g'

g=zeros(datap,1);

for n=1:data
    g(n)=Ttheoig(n);
end

g(data+1)=a(6,1);
a(6,2)=a(6,1);
a(6,3)=a(6,1);
g(data+2)=a(6,4);
g(data+3)=a(6,5);
g(data+4)=a(7,1);
a(7,2)=a(7,1);
a(7,3)=a(7,1);
g(data+5)=a(7,4);
g(data+6)=a(7,5);
g(data+7)=a(7,6);
g(data+8)=a(8,1);
a(8,2)=a(8,1);
a(8,3)=a(8,1);
g(data+9)=a(8,4);
g(data+10)=a(8,5);
g(data+11)=a(8,6);

g(data+12)=a(1,6);
a(2,6)=a(1,6);
a(3,6)=a(1,6);
g(data+13)=a(4,6);
g(data+14)=a(5,6);
g(data+15)=a(1,7);
a(2,7)=a(1,7);
a(3,7)=a(1,7);
g(data+16)=a(4,7);
g(data+17)=a(5,7);
g(data+18)=a(6,7);
g(data+19)=a(1,8);
a(2,8)=a(1,8);
a(3,8)=a(1,8);
g(data+20)=a(4,8);
g(data+21)=a(5,8);
g(data+22)=a(6,8);

g(data+23)=b(6,1);
b(6,2)=b(6,1);
b(6,3)=b(6,1);
g(data+24)=b(6,4);
g(data+25)=b(6,5);
```

```
g(data+26)=b(7,1);
b(7,2)=b(7,1);
b(7,3)=b(7,1);
g(data+27)=b(7,4);
g(data+28)=b(7,5);
g(data+29)=b(7,6);
g(data+30)=b(8,1);
b(8,2)=b(8,1);
b(8,3)=b(8,1);
g(data+31)=b(8,4);
g(data+32)=b(8,5);
g(data+33)=b(8,6);

g(data+34)=b(1,6);
b(2,6)=b(1,6);
b(3,6)=b(1,6);
g(data+35)=b(4,6);
g(data+36)=b(5,6);
g(data+37)=b(1,7);
b(2,7)=b(1,7);
b(3,7)=b(1,7);
g(data+38)=b(4,7);
g(data+39)=b(5,7);
g(data+40)=b(6,7);
g(data+41)=b(1,8);
b(2,8)=b(1,8);
b(3,8)=b(1,8);
g(data+42)=b(4,8);
g(data+43)=b(5,8);
g(data+44)=b(6,8);

%Define lower and upper bounds for
unknowns

A=[];
d=[];
Aeq=[];
beq=[];
lb=zeros(datap,1);

for n=1:data
    lb(n)=340;
end

for n=data+1:data+22
    lb(n)=-30000;
end

for n=data+23:datap
    lb(n)=-100;
end

ub=zeros(datap,1);

for n=1:data
    ub(n)=400;
end

for n=data+1:data+22
    ub(n)=30000;
end

for n=data+23:datap
    ub(n)=100;
end

%Optimization Process, solve for
predicted bubble points and parameters,
store in 'p'

options=optimset('MaxFunEvals',45000);
options=optimset(options,'MaxIter',45000
);
options=optimset(options,'disp','iter','
LargeScale','off','TolFun',.0000000001);
p=fmincon(@udod105,g,A,d,Aeq,beq,lb,ub,@
udod94,options);
```

C.3.2 Objective Function Subprogram

The objective function subprogram for the revision of new parameters for interactions with NaCl and KCl is presented as follows with a file name *udod105*.

```
function f=udod105(g)

%Define number of components, subgroups
and data

comp=6;
subgroup=8;
data=85;

%Define experimental data

P=101325;

X1=[0.631    0.286    0.083
   0.562    0.345    0.093
   0.423    0.516    0.061
   0.486    0.433    0.081
   0.288    0.646    0.066
   0.387    0.519    0.094
   0.39     0.506    0.104
   0.33     0.467    0.203
   0.663    0.007    0.33
   0.83     0.035    0.135
   0.512    0.306    0.182
   0.77     0.049    0.181
   0.729    0.077    0.194
   0.625    0.114    0.261
   0.74     0.007    0.253
   0.457    0.218    0.325
   0.584    0.005    0.411
```

```
    0.436    0.085    0.479];

X2=[0.484    0.477    0.039
    0.536    0.318    0.146
    0.596    0.297    0.107
    0.379    0.576    0.045
    0.478    0.376    0.146
    0.314    0.637    0.049
    0.373    0.555    0.072
    0.393    0.443    0.164
    0.373    0.524    0.103
    0.434    0.427    0.139
    0.42     0.309    0.271
    0.422    0.259    0.319
    0.336    0.492    0.172
    0.337    0.505    0.158
    0.334    0.307    0.359
    0.455    0.218    0.327
    0.424    0.159    0.417
    0.535    0.388    0.077
    0.476    0.46     0.064
    0.476    0.438    0.086
    0.343    0.581    0.076
    0.376    0.528    0.096
    0.32     0.586    0.094
    0.386    0.489    0.125
    0.315    0.594    0.091
    0.288    0.63     0.082
    0.311    0.582    0.107
    0.351    0.52     0.129
    0.277    0.62     0.103
    0.333    0.526    0.141
    0.276    0.626    0.098
    0.358    0.504    0.138
    0.337    0.523    0.14
    0.405    0.373    0.222
    0.339    0.544    0.117
    0.347    0.505    0.148
    0.319    0.498    0.183
    0.353    0.482    0.165
    0.346    0.475    0.179
    0.337    0.492    0.171
    0.326    0.476    0.198
    0.335    0.468    0.197
    0.276    0.581    0.143
    0.339    0.472    0.189
    0.327    0.464    0.209
    0.26     0.555    0.185
    0.326    0.443    0.231
    0.294    0.455    0.251
    0.321    0.427    0.252
    0.314    0.378    0.308
    0.299    0.429    0.272
    0.287    0.375    0.338
    0.348    0.296    0.356
    0.35     0.285    0.365
    0.373    0.234    0.393
    0.272    0.404    0.324
    0.285    0.396    0.319
    0.263    0.4      0.337
    0.246    0.367    0.387
    0.304    0.268    0.428
    0.247    0.371    0.382
    0.207    0.348    0.445
    0.187    0.25     0.563
    0.069    0.359    0.572
    0.166    0.265    0.569
    0.218    0.186    0.596
    0.13     0.191    0.679];

x=zeros(data,comp);

for i=1:18
    x(i,4)=0.1;
    x(i,5)=x(i,4);
    for j=1:3
        x(i,j)=X1(i,j)*(1-2*x(i,4));
    end
    x(i,6)=0;
end

for i=19:data
    x(i,4)=0.1;
    x(i,6)=x(i,4);
    for j=1:3
        x(i,j)=X2(i-18,j)*(1-2*x(i,4));
    end
    x(i,5)=0;
end

yexp1=[0.736    0.246    0.018
       0.7      0.277    0.023
       0.656    0.319    0.025
       0.674    0.302    0.024
       0.603    0.354    0.043
       0.628    0.336    0.036
       0.626    0.336    0.038
       0.544    0.388    0.068
       0.929    0.011    0.06
       0.936    0.045    0.019
       0.679    0.288    0.033
       0.905    0.068    0.027
       0.865    0.106    0.029
       0.789    0.167    0.044
       0.946    0.01     0.044
       0.625    0.302    0.073
       0.902    0.01     0.088
       0.71     0.186    0.104];

yexp2=[0.685    0.302    0.013
       0.683    0.288    0.029
       0.715    0.263    0.022
       0.656    0.324    0.02
       0.653    0.314    0.033
       0.624    0.348    0.028
       0.629    0.339    0.032
       0.605    0.351    0.044
       0.618    0.344    0.038
       0.613    0.345    0.042
       0.598    0.344    0.058
       0.601    0.334    0.065
       0.561    0.378    0.061
       0.553    0.386    0.061
       0.519    0.395    0.086
       0.62     0.301    0.079
       0.628    0.278    0.094
       0.622    0.343    0.035
       0.659    0.32     0.021
       0.671    0.308    0.021
       0.605    0.359    0.036
```

```
        0.633    0.338   0.029
        0.589    0.369   0.042
        0.596    0.361   0.043
        0.58     0.374   0.046
        0.567    0.385   0.048
        0.574    0.38    0.046
        0.576    0.378   0.046
        0.585    0.372   0.043
        0.593    0.367   0.04
        0.573    0.377   0.05
        0.574    0.375   0.051
        0.557    0.388   0.055
        0.596    0.359   0.045
        0.558    0.387   0.055
        0.562    0.384   0.054
        0.516    0.416   0.068
        0.556    0.386   0.058
        0.542    0.398   0.06
        0.525    0.408   0.067
        0.462    0.443   0.095
        0.471    0.442   0.087
        0.544    0.395   0.061
        0.53     0.404   0.066
        0.532    0.403   0.065
        0.545    0.398   0.057
        0.514    0.414   0.072
        0.504    0.422   0.074
        0.453    0.454   0.093
        0.528    0.408   0.064
        0.489    0.432   0.079
        0.502    0.425   0.073
        0.516    0.396   0.08
        0.522    0.392   0.086
        0.534    0.377   0.089
        0.461    0.451   0.088
        0.383    0.497   0.12
        0.489    0.435   0.076
        0.42     0.476   0.104
        0.468    0.421   0.111
        0.432    0.466   0.102
        0.357    0.51    0.133
        0.344    0.51    0.146
        0.173    0.612   0.215
        0.315    0.528   0.157
        0.406    0.441   0.153
        0.275    0.522   0.203];

yexp=zeros(data,3);

for i=1:18
    for j=1:3
        yexp(i,j)=yexp1(i,j);
    end
end

for i=19:data
    for j=1:3
        yexp(i,j)=yexp2(i-18,j);
    end
end

%Define Rk, Qk, and vk values

R=[0.6325;0.6325;0.6325;1.2302;1.7334;0.
9861;3;3];
Q=[1.0608;0.7081;0.3554;0.8927;2.4561;0.
9917;3;3];
v=[1 0 1 0 0 0;
   1 0 3 0 0 0;
   0 0 0 0 0 0;
   1 0 1 0 0 0;
   0 1 0 0 0 0;
   0 0 0 1 0 0;
   0 0 0 0 1 0;
   0 0 0 0 0 1];

r=zeros(comp,1);
q=zeros(comp,1);

for i=1:comp
    for k=1:subgroup
        r(i)=r(i)+R(k)*v(k,i);
        q(i)=q(i)+Q(k)*v(k,i);
    end
end

%Define binary interaction parameters

a=[0 0 0 2777 1391.3 6731.4 6767.4 -
2071.6;
   0 0 0 2777 1391.3 6731.4 6767.4 -
2071.6;
   0 0 0 2777 1391.3 6731.4 6767.4 -
2071.6;
   1606 1606 1606 0 -801.9 4286.2 -
7007.6 -5941.1;
   -17.253 -17.253 -17.253 1460 0 5.3069
-1970.2 -5616.8;
   -7424.5 -7424.5 -7424.5 4950.2 -
144.82 0 -2425.8 -6110.8;
   -1899 -1899 -1899 -2974.7 -552.42
23275 0 1000;
   12803 12803 12803 399.74 -481.55
18.581 1000 0];
b=[0 0 0 -4.674 -3.6156 47 49.151 0.228;
   0 0 0 -4.674 -3.6156 47 49.151 0.228;
   0 0 0 -4.674 -3.6156 47 49.151 0.228;
   -4.746 -4.746 -4.746 0 3.824 -62.547
14.053 0.0032;
   0.8389 0.8389 0.8389 -8.673 0 0.4377
1.2864 0.4801;
   20.728 20.728 20.728 -15.522 -0.0174
0 0.0221 0;
   72.291 72.291 72.291 8.1759 -0.0097
2.224 0 1;
   5.1318 5.1318 5.1318 0.0053 -0.0051 0
1 0];
c=[0 0 0 0.001551 0.001144 0 0 0;
   0 0 0 0.001551 0.001144 0 0 0;
   0 0 0 0.001551 0.001144 0 0 0;
   0.0009181 0.0009181 0.0009181 0 -
0.007514 0 0 0;
   0.0009021 0.0009021 0.0009021 0.01641
0 0 0 0;
   0 0 0 0 0 0 0 0;
   0 0 0 0 0 0 0 0;
   0 0 0 0 0 0 0 0];

%Define unknowns as 'g'
```

```
Ttheo=zeros(data,1);

for n=1:data
    Ttheo(n)=g(n);
end

a(6,1)=g(data+1);
a(6,2)=a(6,1);
a(6,3)=a(6,1);
a(6,4)=g(data+2);
a(6,5)=g(data+3);
a(7,1)=g(data+4);
a(7,2)=a(7,1);
a(7,3)=a(7,1);
a(7,4)=g(data+5);
a(7,5)=g(data+6);
a(7,6)=g(data+7);
a(8,1)=g(data+8);
a(8,2)=a(8,1);
a(8,3)=a(8,1);
a(8,4)=g(data+9);
a(8,5)=g(data+10);
a(8,6)=g(data+11);

a(1,6)=g(data+12);
a(2,6)=a(1,6);
a(3,6)=a(1,6);
a(4,6)=g(data+13);
a(5,6)=g(data+14);
a(1,7)=g(data+15);
a(2,7)=a(1,7);
a(3,7)=a(1,7);
a(4,7)=g(data+16);
a(5,7)=g(data+17);
a(6,7)=g(data+18);
a(1,8)=g(data+19);
a(2,8)=a(1,8);
a(3,8)=a(1,8);
a(4,8)=g(data+20);
a(5,8)=g(data+21);
a(6,8)=g(data+22);

b(6,1)=g(data+23);
b(6,2)=b(6,1);
b(6,3)=b(6,1);
b(6,4)=g(data+24);
b(6,5)=g(data+25);
b(7,1)=g(data+26);
b(7,2)=b(7,1);
b(7,3)=b(7,1);
b(7,4)=g(data+27);
b(7,5)=g(data+28);
b(7,6)=g(data+29);
b(8,1)=g(data+30);
b(8,2)=b(8,1);
b(8,3)=b(8,1);
b(8,4)=g(data+31);
b(8,5)=g(data+32);
b(8,6)=g(data+33);

b(1,6)=g(data+34);
b(2,6)=b(1,6);
b(3,6)=b(1,6);
b(4,6)=g(data+35);
b(5,6)=g(data+36);
b(1,7)=g(data+37);
b(2,7)=b(1,7);
b(3,7)=b(1,7);
b(4,7)=g(data+38);
b(5,7)=g(data+39);
b(6,7)=g(data+40);
b(1,8)=g(data+41);
b(2,8)=b(1,8);
b(3,8)=b(1,8);
b(4,8)=g(data+42);
b(5,8)=g(data+43);
b(6,8)=g(data+44);

%Calculation of activity coefficients
using UNIFAC Dortmund model

e=zeros(subgroup,comp);

for i=1:comp
    for k=1:subgroup
        e(k,i)=v(k,i)*Q(k)/q(i);
    end
end

tau=zeros(subgroup,subgroup,data);

for n=1:data
    for k=1:subgroup
        for m=1:subgroup
            tau(m,k,n)=exp(-
(a(m,k)+b(m,k)*Ttheo(n)+c(m,k)*Ttheo(n)^
2)/Ttheo(n));
        end
    end
end

B=zeros(subgroup,comp,data);

for n=1:data
    for i=1:comp
        for k=1:subgroup
            for m=1:subgroup

B(k,i,n)=B(k,i,n)+e(m,i)*tau(m,k,n);
            end
        end
    end
end

numtheta=zeros(subgroup,data);
denomtheta=zeros(subgroup,data);
theta=zeros(subgroup,data);

for n=1:data
    for k=1:subgroup
        for i=1:comp

numtheta(k,n)=numtheta(k,n)+x(n,i)*q(i)*
e(k,i);

denomtheta(k,n)=denomtheta(k,n)+x(n,i)*q
(i);

theta(k,n)=numtheta(k,n)/denomtheta(k,n)
;
```

```
        end
    end
end

s=zeros(subgroup,data);

for n=1:data
    for k=1:subgroup
        for m=1:subgroup

s(k,n)=s(k,n)+theta(m,n)*tau(m,k,n);
        end
    end
end

sum=zeros(comp,data);

for n=1:data
    for i=1:comp
        for k=1:subgroup

sum(i,n)=sum(i,n)+theta(k,n)*B(k,i,n)/s(
k,n)-e(k,i)*log(B(k,i,n)/s(k,n));
        end
    end
end

denomJ=zeros(comp,data);
denomJmod=zeros(comp,data);
denomL=zeros(comp,data);
J=zeros(comp,data);
Jmod=zeros(comp,data);
L=zeros(comp,data);

for n=1:data
    for i=1:comp
        for j=1:comp

denomJ(i,n)=denomJ(i,n)+r(j)*x(n,j);
            J(i,n)=r(i)/denomJ(i,n);

denomJmod(i,n)=denomJmod(i,n)+r(j)^0.75*
x(n,j);

Jmod(i,n)=r(i)^0.75/denomJmod(i,n);

denomL(i,n)=denomL(i,n)+q(j)*x(n,j);
            L(i,n)=q(i)/denomL(i,n);
        end
    end
end

lngammaR=zeros(comp,data);
lngammaC=zeros(comp,data);
gammatheo=zeros(comp,data);

for n=1:data
    for i=1:comp
        lngammaR(i,n)=q(i)*(1-sum(i,n));
        lngammaC(i,n)=1-
Jmod(i,n)+log(Jmod(i,n))-5*q(i)*(1-
J(i,n)/L(i,n)+log(J(i,n)/L(i,n)));

gammatheo(i,n)=exp(lngammaR(i,n)+lngamma
C(i,n));
    end
end

%Calculation of vapor mole fraction
values

Psattheo=zeros(3,data);

for m=1:data
    Psattheo(1,m)=100000*exp(12.2917-
3803.98/(Ttheo(m)-41.68));
    Psattheo(2,m)=100000*exp(11.6834-
3816.44/(Ttheo(m)-46.13));
    Psattheo(3,m)=100000*exp(10.5958-
3137.02/(Ttheo(m)-94.43));
end

ytheo=zeros(data,3);

for m=1:data
    for j=1:3

ytheo(m,j)=gammatheo(j,m)*x(m,j)*Psatthe
o(j,m)/P;
    end
end

%Define objective function

f=0;
for n=1:data
    f=f+((yexp(n,1)-
ytheo(n,1))/yexp(n,1))^2;
    f=f+((yexp(n,3)-
ytheo(n,3))/yexp(n,3))^2;
end
```

C.3.3 UNIFAC Dortmund Model Subprogram

The UNIFAC Dortmund model subprogram for the revision of new parameters for interactions with NaCl and KCl is presented as follows with a file name *udod94*.

```
function [cineq,ceq]=udod94(g)

%Define number of components, subgroups
and data

comp=6;
subgroup=8;
data=85;

%Define experimental data

P=101325;

X1=[0.631   0.286   0.083
   0.562    0.345   0.093
   0.423    0.516   0.061
   0.486    0.433   0.081
   0.288    0.646   0.066
   0.387    0.519   0.094
   0.39     0.506   0.104
   0.33     0.467   0.203
   0.663    0.007   0.33
   0.83     0.035   0.135
   0.512    0.306   0.182
   0.77     0.049   0.181
   0.729    0.077   0.194
   0.625    0.114   0.261
   0.74     0.007   0.253
   0.457    0.218   0.325
   0.584    0.005   0.411
   0.436    0.085   0.479];

X2=[0.484   0.477   0.039
   0.536    0.318   0.146
   0.596    0.297   0.107
   0.379    0.576   0.045
   0.478    0.376   0.146
   0.314    0.637   0.049
   0.373    0.555   0.072
   0.393    0.443   0.164
   0.373    0.524   0.103
   0.434    0.427   0.139
   0.42     0.309   0.271
   0.422    0.259   0.319
   0.336    0.492   0.172
   0.337    0.505   0.158
   0.334    0.307   0.359
   0.455    0.218   0.327
   0.424    0.159   0.417
   0.535    0.388   0.077
   0.476    0.46    0.064
   0.476    0.438   0.086
   0.343    0.581   0.076
   0.376    0.528   0.096
   0.32     0.586   0.094
   0.386    0.489   0.125
   0.315    0.594   0.091
   0.288    0.63    0.082
   0.311    0.582   0.107
   0.351    0.52    0.129
   0.277    0.62    0.103
   0.333    0.526   0.141
   0.276    0.626   0.098
   0.358    0.504   0.138
   0.337    0.523   0.14
   0.405    0.373   0.222
   0.339    0.544   0.117
   0.347    0.505   0.148
   0.319    0.498   0.183
   0.353    0.482   0.165
   0.346    0.475   0.179
   0.337    0.492   0.171
   0.326    0.476   0.198
   0.335    0.468   0.197
   0.276    0.581   0.143
   0.339    0.472   0.189
   0.327    0.464   0.209
   0.26     0.555   0.185
   0.326    0.443   0.231
   0.294    0.455   0.251
   0.321    0.427   0.252
   0.314    0.378   0.308
   0.299    0.429   0.272
   0.287    0.375   0.338
   0.348    0.296   0.356
   0.35     0.285   0.365
   0.373    0.234   0.393
   0.272    0.404   0.324
   0.285    0.396   0.319
   0.263    0.4     0.337
   0.246    0.367   0.387
   0.304    0.268   0.428
   0.247    0.371   0.382
   0.207    0.348   0.445
   0.187    0.25    0.563
   0.069    0.359   0.572
   0.166    0.265   0.569
   0.218    0.186   0.596
   0.13     0.191   0.679];

x=zeros(data,comp);

for i=1:18
    x(i,4)=0.1;
    x(i,5)=x(i,4);
    for j=1:3
        x(i,j)=X1(i,j)*(1-2*x(i,4));
    end
    x(i,6)=0;
end

for i=19:data
    x(i,4)=0.1;
    x(i,6)=x(i,4);
```

```
    for j=1:3
        x(i,j)=X2(i-18,j)*(1-2*x(i,4));
    end
    x(i,5)=0;
end

%Define Rk, Qk, and vk values

R=[0.6325;0.6325;0.6325;1.2302;1.7334;0.
9861;3;3];
Q=[1.0608;0.7081;0.3554;0.8927;2.4561;0.
9917;3;3];
v=[1 0 1 0 0 0;
   1 0 3 0 0 0;
   0 0 0 0 0 0;
   1 0 1 0 0 0;
   0 1 0 0 0 0;
   0 0 0 1 0 0;
   0 0 0 0 1 0;
   0 0 0 0 0 1];

r=zeros(comp,1);
q=zeros(comp,1);

for i=1:comp
    for k=1:subgroup
        r(i)=r(i)+R(k)*v(k,i);
        q(i)=q(i)+Q(k)*v(k,i);
    end
end

%Define binary interaction parameters

a=[0 0 0 2777 1391.3 6731.4 6767.4 -
2071.6;
   0 0 0 2777 1391.3 6731.4 6767.4 -
2071.6;
   0 0 0 2777 1391.3 6731.4 6767.4 -
2071.6;
   1606 1606 1606 0 -801.9 4286.2 -
7007.6 -5941.1;
   -17.253 -17.253 -17.253 1460 0 5.3069
-1970.2 -5616.8;
   -7424.5 -7424.5 -7424.5 4950.2 -
144.82 0 -2425.8 -6110.8;
   -1899 -1899 -1899 -2974.7 -552.42
23275 0 1000;
   12803 12803 12803 399.74 -481.55
18.581 1000 0];
b=[0 0 0 -4.674 -3.6156 47 49.151 0.228;
   0 0 0 -4.674 -3.6156 47 49.151 0.228;
   0 0 0 -4.674 -3.6156 47 49.151 0.228;
   -4.746 -4.746 -4.746 0 3.824 -62.547
14.053 0.0032;
   0.8389 0.8389 0.8389 -8.673 0 0.4377
1.2864 0.4801;
   20.728 20.728 20.728 -15.522 -0.0174
0 0.0221 0;
   72.291 72.291 72.291 8.1759 -0.0097
2.224 0 1;
   5.1318 5.1318 5.1318 0.0053 -0.0051 0
1 0];
c=[0 0 0 0.001551 0.001144 0 0 0;
   0 0 0 0.001551 0.001144 0 0 0;
   0 0 0 0.001551 0.001144 0 0 0;
   0.0009181 0.0009181 0.0009181 0 -
0.007514 0 0 0;
   0.0009021 0.0009021 0.0009021 0.01641
0 0 0 0;
   0 0 0 0 0 0 0 0;
   0 0 0 0 0 0 0 0;
   0 0 0 0 0 0 0 0];

%Define unknowns as 'g'

Ttheo=zeros(data,1);

for n=1:data
    Ttheo(n)=g(n);
end

a(6,1)=g(data+1);
a(6,2)=a(6,1);
a(6,3)=a(6,1);
a(6,4)=g(data+2);
a(6,5)=g(data+3);
a(7,1)=g(data+4);
a(7,2)=a(7,1);
a(7,3)=a(7,1);
a(7,4)=g(data+5);
a(7,5)=g(data+6);
a(7,6)=g(data+7);
a(8,1)=g(data+8);
a(8,2)=a(8,1);
a(8,3)=a(8,1);
a(8,4)=g(data+9);
a(8,5)=g(data+10);
a(8,6)=g(data+11);

a(1,6)=g(data+12);
a(2,6)=a(1,6);
a(3,6)=a(1,6);
a(4,6)=g(data+13);
a(5,6)=g(data+14);
a(1,7)=g(data+15);
a(2,7)=a(1,7);
a(3,7)=a(1,7);
a(4,7)=g(data+16);
a(5,7)=g(data+17);
a(6,7)=g(data+18);
a(1,8)=g(data+19);
a(2,8)=a(1,8);
a(3,8)=a(1,8);
a(4,8)=g(data+20);
a(5,8)=g(data+21);
a(6,8)=g(data+22);

b(6,1)=g(data+23);
b(6,2)=b(6,1);
b(6,3)=b(6,1);
b(6,4)=g(data+24);
b(6,5)=g(data+25);
b(7,1)=g(data+26);
b(7,2)=b(7,1);
b(7,3)=b(7,1);
b(7,4)=g(data+27);
b(7,5)=g(data+28);
b(7,6)=g(data+29);
b(8,1)=g(data+30);
b(8,2)=b(8,1);
```

```
b(8,3)=b(8,1);
b(8,4)=g(data+31);
b(8,5)=g(data+32);
b(8,6)=g(data+33);

b(1,6)=g(data+34);
b(2,6)=b(1,6);
b(3,6)=b(1,6);
b(4,6)=g(data+35);
b(5,6)=g(data+36);
b(1,7)=g(data+37);
b(2,7)=b(1,7);
b(3,7)=b(1,7);
b(4,7)=g(data+38);
b(5,7)=g(data+39);
b(6,7)=g(data+40);
b(1,8)=g(data+41);
b(2,8)=b(1,8);
b(3,8)=b(1,8);
b(4,8)=g(data+42);
b(5,8)=g(data+43);
b(6,8)=g(data+44);

%Calculation of activity coefficients
using UNIFAC Dortmund model

e=zeros(subgroup,comp);

for i=1:comp
    for k=1:subgroup
        e(k,i)=v(k,i)*Q(k)/q(i);
    end
end

tau=zeros(subgroup,subgroup,data);

for n=1:data
    for k=1:subgroup
        for m=1:subgroup
            tau(m,k,n)=exp(-
(a(m,k)+b(m,k)*Ttheo(n)+c(m,k)*Ttheo(n)^
2)/Ttheo(n));
        end
    end
end

B=zeros(subgroup,comp,data);

for n=1:data
    for i=1:comp
        for k=1:subgroup
            for m=1:subgroup

B(k,i,n)=B(k,i,n)+e(m,i)*tau(m,k,n);
            end
        end
    end
end

numtheta=zeros(subgroup,data);
denomtheta=zeros(subgroup,data);
theta=zeros(subgroup,data);

for n=1:data
    for k=1:subgroup
        for i=1:comp

numtheta(k,n)=numtheta(k,n)+x(n,i)*q(i)*
e(k,i);

denomtheta(k,n)=denomtheta(k,n)+x(n,i)*q
(i);

theta(k,n)=numtheta(k,n)/denomtheta(k,n)
;
        end
    end
end

s=zeros(subgroup,data);

for n=1:data
    for k=1:subgroup
        for m=1:subgroup

s(k,n)=s(k,n)+theta(m,n)*tau(m,k,n);
        end
    end
end

sum=zeros(comp,data);

for n=1:data
    for i=1:comp
        for k=1:subgroup

sum(i,n)=sum(i,n)+theta(k,n)*B(k,i,n)/s(
k,n)-e(k,i)*log(B(k,i,n)/s(k,n));
        end
    end
end

denomJ=zeros(comp,data);
denomJmod=zeros(comp,data);
denomL=zeros(comp,data);
J=zeros(comp,data);
Jmod=zeros(comp,data);
L=zeros(comp,data);

for n=1:data
    for i=1:comp
        for j=1:comp

denomJ(i,n)=denomJ(i,n)+r(j)*x(n,j);
            J(i,n)=r(i)/denomJ(i,n);

denomJmod(i,n)=denomJmod(i,n)+r(j)^0.75*
x(n,j);

Jmod(i,n)=r(i)^0.75/denomJmod(i,n);

denomL(i,n)=denomL(i,n)+q(j)*x(n,j);
            L(i,n)=q(i)/denomL(i,n);
        end
    end
end

lngammaR=zeros(comp,data);
lngammaC=zeros(comp,data);
gammatheo=zeros(comp,data);
```

```
for n=1:data
    for i=1:comp
        lngammaR(i,n)=q(i)*(1-sum(i,n));
        lngammaC(i,n)=1-
Jmod(i,n)+log(Jmod(i,n))-5*q(i)*(1-
J(i,n)/L(i,n)+log(J(i,n)/L(i,n)));

gammatheo(i,n)=exp(lngammaR(i,n)+lngamma
C(i,n));
    end
end

%Calculation of vapor mole fraction
values

Psattheo=zeros(3,data);

for m=1:data
    Psattheo(1,m)=100000*exp(12.2917-
3803.98/(Ttheo(m)-41.68));
    Psattheo(2,m)=100000*exp(11.6834-
3816.44/(Ttheo(m)-46.13));
    Psattheo(3,m)=100000*exp(10.5958-
3137.02/(Ttheo(m)-94.43));
end

ytheo=zeros(data,3);

for m=1:data
    for j=1:3

ytheo(m,j)=gammatheo(j,m)*x(m,j)*Psatthe
o(j,m)/P;
    end
end

%Define constraints, sum of y equal to 1

cineq=[];
ceq=zeros(1,data);

for m=1:data

ceq(m)=ytheo(m,1)+ytheo(m,2)+ytheo(m,3)-
1;
end
```