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APPENDICES

APPENDIX A: The Samples of Calculation

A.1 Solubility Parameter Prediction in Table 4.8

Since the solubility space of asphaltene is assumed as a pseudo-sphere shape (spheroid: the ellipsoid that the radiuses of two axes are the same). The distance between the center point that is the solubility parameter of asphaltene solubility spheroid, and the points at the surface of spheroid should follow the Equation (A.1).

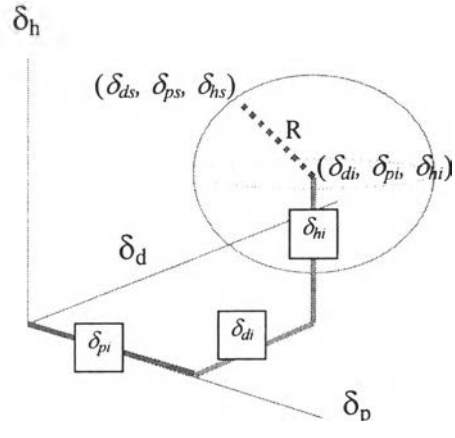

Figure A.1 The model of solubility spheroid.

From the spheroid equation,

$$\left(\delta_{d,i}-\delta_{d,s}\right)^2+b\left(\delta_{p,i}-\delta_{p,s}\right)^2+b\left(\delta_{h,i}-\delta_{h,s}\right)^2=R_d^2 \qquad \text{(A.1)}$$

where i is denoted as at the asphaltene

s is denoted as the point at the surface of solubility spheroid

b is the weighting factor equal to 0.25 (Hansen, 2000)

The solubility parameters at the surface of solubility spheroid were obtained from the experimental data and Equation (4.2). The prediction procedure is shown below:

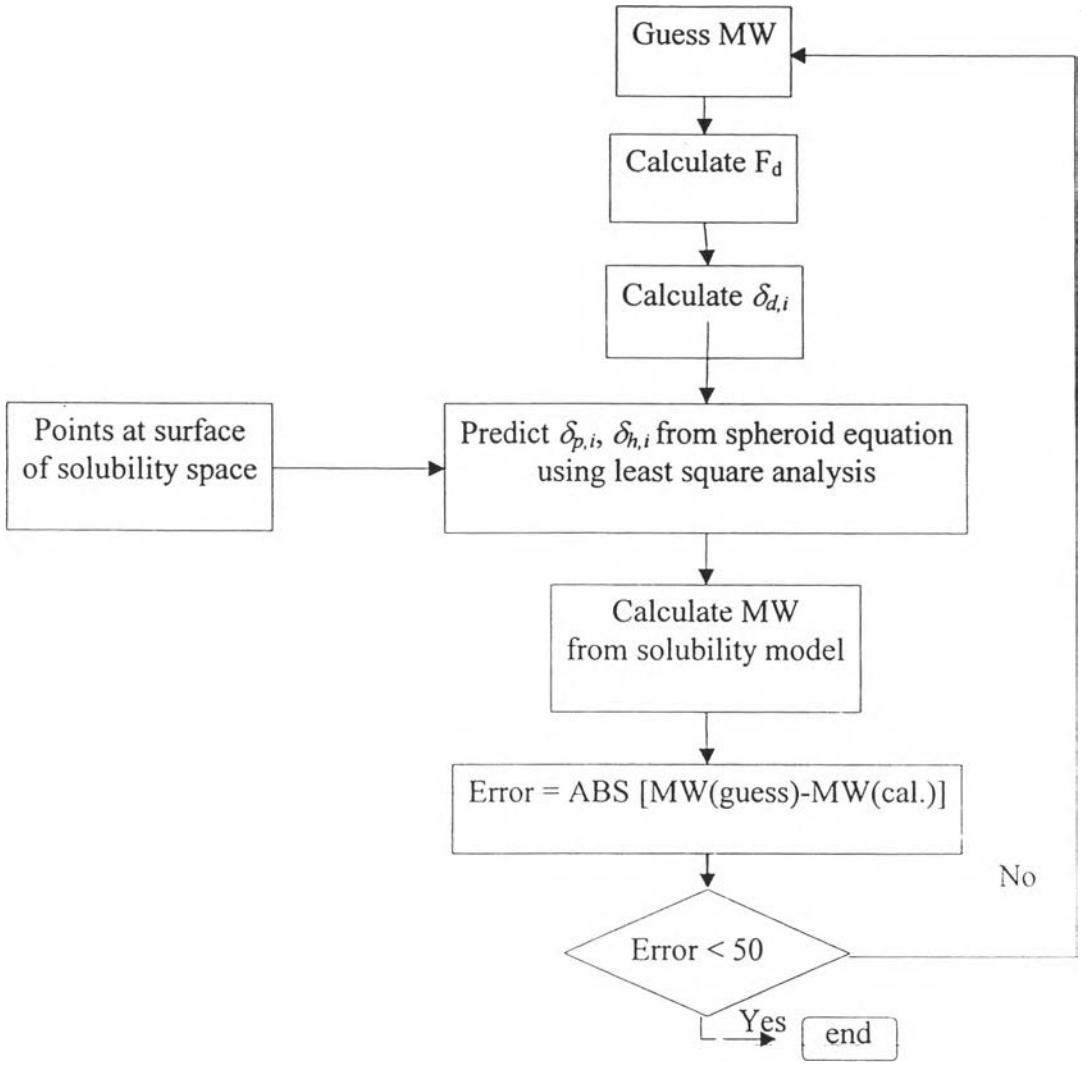

Figure A.2 Three-component solubility parameter prediction procedure.

Using the least square analysis with the constraints from the fractionation procedure as expressed below:

Unfractionated Cold Lake:

$$0 < \delta_{pi} < 30$$

F40/60 Fraction

$$2.52 < \delta_{pi} < 30$$

F30/70 Fraction

$$1.89 < \delta_{pi} < 2.52$$

F20/80 Fraction

$$1.26 < \delta_{pi} < 1.89$$

F10/90 Fraction

$$0 < \delta_{pi} < 1.26$$

A.2 Molecular Weight Prediction

Predicted molecular weight at certain percent toluene in heptane can be determined by Equation (2.10) and experimental solubility data. Equilibrium ratio (K) in Equation (2.10) was obtained from Equation (2.5) and (2.6) for single and three-component solubility parameter model, respectively. Once, these predicted molecular weights were plotted with percentage toluene in heptane and extrapolated to zero and a hundred percent. The predicted molecular weights that were obtained from extrapolation were reported in Table 4.9.

Sample of calculation: for unfractionated Cold Lake asphaltene at 30% toluene in heptane

A.2.1 Single-Component Solubility Model

Put all properties of asphaltene; density of asphaltene = 1259.1 kg/m^3 and solubility parameter = 22.49 MPa$^{0.5}$, and the properties of solvent mixture at particular percent toluene in binary solvent in the Maple program (analytical solving program) which shows in next section.

Once, the molecular weights of asphaltene were plotted as a function of percent toluene in heptane as shown in Figure 4.16. From that plot, the molecular weights of asphaltene at zero and a hundred percent toluene in heptane were determined using the correlation below:

$$MW = 1.7\,(\%\text{toluene in heptane}) + 850.07$$

The molecular weights that were obtained from this equation are 850 and 1020 g/mol.

A.2.2 Three-Component Solubility Model

The same calculation procedure was used for the three-component solubility parameters except value of solubility parameters. In this case, the solubility

parameters (Table 5.8) are 21.12, 1.0639 and 7.1159 $MPa^{0.5}$ for dispersive, polar and hydrogen bonding force, respectively.

Then the molecular weights of asphaltene at zero and a hundred percent toluene in heptane were determined using the correlation in Figure 4.17 as indicated below:

$$MW = 10.307\ (\%\text{toluene in heptane}) + 977.82$$

The molecular weights that were obtained from this equation are 978 and 2009 g/mol.

APPENDIX B: Analytical Solving Program (Maple 8)

B.1 Molecular Weight Determination Program of Single component solubility parameter model

Program 1

```
restart;
parameters:={R=8.314,T=298,vm=1.32e-4,deltai=22.49,deltam=16.17,rho=1259.1,
 moleT=0.3/1.06e-4,moleH=0.70/1.46e-4,Cas=0.9302e3};
```

$$parameters := \{R = 8.314,\ T = 298,\ deltai = 22.49,\ \rho = 1259.1,\ vm = 0.000132,\ deltam = 16.17,\ moleT = 2830.188679,\ moleH = 4794.520548,\ Cas = 930.2\}$$

```
eqn1a:=1000*vil*rho*(moleT+moleH)/Cas+1=exp(1-vil/vm+ln(vil/vm)
+1000000*vil/R/T*(deltai-deltam)^2);
```

$$eqn1a := \frac{1000\ vil\ \rho\ (moleT + moleH)}{Cas} + 1 = e^{\left(1 - \frac{vil}{vm} + \ln\left(\frac{vil}{vm}\right) + \frac{1000000\ vil\ (deltai - deltam)^2}{R\ T}\right)}$$

```
eqn1:=eval(eqn1a,parameters);
```

$$eqn1 := 0.1032065296\ 10^8\ vil + 1 = e^{(1. + 8545.832434\ vil + \ln(7575.757576\ vil))}$$

```
solution:=solve({eqn1},{vil});
```

$$solution := \{vil = 0.0007274987168\}$$

```
mw:=eval(eval(vil,solution)*rho*1000,parameters);
```

$$mw := 915.9936343$$

B.2 Molecular Weight Determination Program of Three component solubility parameters model

Program 2

```
restart;
eqn:=1000*vil*rho*(moleT+moleH)/Cas+1=exp(1-vil/vm+ln(vil/vm)
+1000000*vil/R/T*((deltadi-deltadm)^2+0.25*((deltahi-deltahm)^2+(deltapi-
deltapm)^2)));
```

$$eqn := \frac{1000\ vil\ \rho\ (moleT + moleH)}{Cas} + 1 = e^{\left(1 - \frac{vil}{vm} + \ln\left(\frac{vil}{vm}\right) + \frac{1000000\ vil\ ((deltadi - deltadm)^2 + 0.25\ (deltahi - deltahm)^2 + 0.25\ (deltapi - deltapm)^2)}{R\,T}\right)}$$

```
parameters:={R=8.314,T=298,vm=1.32e-4,deltadi=21.12,deltadm=16.30,
deltahi=7.1159,deltahm=0.74,deltapi=1.0639,deltapm=0.52,rho=1259.1,moleT=0.30/
1.06e-4,moleH=0.7/1.46e-4,Cas=0.9302e3};eqn1:=eval(eqn,parameters);
```

$$parameters := \{R = 8.314,\ T = 298,\ vm = 0.000132,\ deltadi = 21.12,\ deltadm = 16.30,\ deltahi = 7.1159,\ deltahm = 0.74,\ deltapi = 1.0639,\ deltapm = 0.52,\ \rho = 1259.1,\ moleT = 2830.188679,\ moleH = 4794.520548,\ Cas = 930.2\}$$

$$eqn1 := 0.1032065296\ 10^8\ vil + 1 = e^{(1. + 5933.186664\ vil + \ln(7575.757576\ vil))}$$

```
solution:=solve({eqn1},{vil});
```

$$solution := \{vil = 0.001047841871\}$$

```
mw:=(eval(vil,solution)*1000*1259.1);
```

$$mw := 1319.337700$$

B.3 Asphaltene Solubility Parameters Determination Program

Program 3: Search

```
clear all;

global dds dps dhs delta_d a

data_fixB;

options = optimset('MaxFunEvals',10000, ...
                'TolFun', 1e-12, ...
                'TolX', 1e-12, ...
                'Display', 'off');

% Make a starting guess at the solution
p0 = [1 1 1];

% lower bound
lb = [0
      0
      0];

% upper bound
ub =  [30
       30
       30];

[p,resnorm] = lsqnonlin(@myfun_fixB,p0,lb,ub,options);

vil = fzero('eqn_fixB',2e-3,options,p,delta_d)

B=a

dp=p(1)

dh=p(2)

R=p(3)

sum_of_err_sqrs=resnorm

mw = vil*1000*1259.1
```

Program 4: Myfun

```
function E = myfun(p)

global dds dps dhs delta_d

E = p(3)^2 - (delta_d-dds).^2 - a*(p(1)-dps).^2 - a*(p(2)-dhs).^2;
```

APPENDIX C: The Values of Model Parameters and Solubility Data of Asphaltene in Toluene/Heptane System

C.1 Parameters of Single Component Solubility Parameter Model

Basis 1 m^3 toluene/heptane solvent mixture

$\delta_{heptane}$	=	15.3	$Mpa^{0.5}$
$V_{heptane}$	=	1.46E-04	m^3/mol
$\delta_{toluene}$	=	18.2	$Mpa^{0.5}$
$V_{toluene}$	=	1.06E-04	m^3/mol
$Density_{asph}$	=	1259.1	kg/m^3
δ_{asph}	=	22.49	$Mpa^{0.5}$
R	=	8.314	J/mol*K
T	=	298	K

Table C.1 The parameter values of single component solubility parameter model

% Toluene	Mole_tolene	Mole_hepane	Mole_total	V_m	δm
0	0	6826.35	6826.35	1.46E-04	15.30
5	470.68	6485.03	6955.71	1.44E-04	15.45
10	941.37	6143.71	7085.08	1.41E-04	15.59
15	1412.05	5802.40	7214.45	1.39E-04	15.74
20	1882.74	5461.08	7343.81	1.36E-04	15.88
25	2353.42	5119.76	7473.18	1.34E-04	16.03
30	2824.10	4778.44	7602.55	1.32E-04	16.17

C.2 Parameters of Three Component Solubility Parameters Model

Basis 1 m^3 toluene/heptane solvent mixture

$\delta_{heptane}$	=	15.3	$Mpa^{0.5}$
$V_{heptane}$	=	1.46E-04	m^3/mol
$\delta_{toluene}$	=	18.2	$Mpa^{0.5}$
$V_{toluene}$	=	1.06E-04	m^3/mol
$Density_{asph}$	=	1259.1	kg/m^3
R	=	8.314	J/mol*K
T	=	298	K

Table C.2 The parameter values of three component solubility parameter model

%Toluene	Mole toluene	Mole heptane	Mole total	V_m	δ_{md}	δ_{mp}	δ_{mh}
0	0	6826.35	6826.35	1.46E-04	15.30	0	0
5	470.68	6485.03	6955.71	1.44E-04	15.48	0.09	0.14
10	941.37	6143.71	7085.08	1.41E-04	15.66	0.19	0.27
15	1412.05	5802.40	7214.45	1.39E-04	15.83	0.27	0.39
20	1882.74	5461.08	7343.81	1.36E-04	15.99	0.36	0.51
25	2353.42	5119.76	7473.18	1.34E-04	16.15	0.44	0.63
30	2824.10	4778.44	7602.55	1.32E-04	16.30	0.52	0.74

C.3 Solubility of Unfractionated Cold Lake Asphaltene and its Fractionated Components

Table C.3 Solubility of Cold Lake asphaltene

% Toluene	Solubility ($C_{A,s}$) (g/dm^3)				
	F40/60	F30/70	F20/80	F10/90	Unfractionate
0	0	0	0.0212	0.1812	0.0279
5	0.0219	0.0245	0.0556	0.3184	0.0650
10	0.0360	0.0436	0.1132	0.6754	0.1097
15	0.0595	0.0727	0.2188	1.3748	0.1707
20	0.0982	0.1214	0.4306	2.6619	0.3090
25	0.1699	0.2096	0.8651	4.5984	0.5347
30	0.2844	0.3580	1.4580	7.9087	0.8773

APPENDIX D: The solubility space of Unfractionated Cold Lake asphaltene

Table D.1 The solubility parameter of pure solvents

No	Solvent	Solubility Parameter ($MPa^{1/2}$)			
		δ_d	δ_p	δ_h	δ_t
1	Pentane	14.5	0	0	14.50
2	Hexane	14.9	0	0	14.90
3	Methanol	15.1	12.3	22.3	29.61
4	Heptane	15.3	0	0	15.30
5	Acetonitrile	15.3	18	6.1	24.40
6	Acetone	15.5	10.4	7	19.94
7	2-Propanol	15.8	6.1	16.4	23.58
8	Ethanol	15.8	8.8	19.4	26.52
9	Dodecane	16	0	0	16.00
10	Allyl Alcohol	16.2	10.8	16.8	25.72
11	1,3-Butanediol	16.6	10	21.5	28.94
12	Ethylene glycol	17	11	26	32.95
13	Glycerol	17.4	12.1	29.3	36.16
14	Nonylphenol	16.5	4.1	9.2	19.33
15	Nitrobenzene/Heptane	15.65	0.64	0.31	15.67
16	Heptane/Toluene	15.77	0.24	0.34	15.78
17	Toluene/Acetone	16.12	8.17	5.76	18.97
18	Nitrobenzene/Acetone	16.38	10.05	6.43	20.26
19	Toluene/Methanol	16.41	7.38	13.14	22.28
20	Toluene/Allyl Alcohol	16.69	8.24	12.76	22.57
21	Tetrahydrofuran	16.8	5.7	8	19.46
22	Decahydronaphthalene	18	0	0	18.00
23	Toluene	18	1.4	2	18.16
24	Methylene Chloride	18.2	6.3	6.1	20.20

25	Acetophenone	19.6	8.6	3.7	21.72
26	Thiophenol	20	4.5	10.3	22.94
27	Nitrobenzene	20	8.6	4.1	22.15
28	Carbondisulfide	20.5	0	0.6	20.51
29	Bromobenzene	20.5	5.5	4.1	21.62
30	1-Methyl naphthalene	20.7	0.8	4.7	21.24

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