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APPENDICES

APPENDIX A Calculation and Samples of Calculation

A1 Calculations of Amount of Metal Loading on NaY Zeolite

A1.1 Amount of Metal Loading on NaY Zeolite

From

$$C_{i2} = C_{i1} * T$$

$$M = C_{i2} * V_0 * 10^{-6}$$

$$\%Wt = \frac{M}{A_0} * 100$$

(A1.1.1)

Where,

C_{i2} = Concentration before dilution (μg/ml)

C_{i1} = Concentration after dilution of metal solution (μg/ml)

T = Times of dilution

M = Amount of metal loading on NaY zeolite (g)

V_0 = Initial volume of metal solution (ml)

%Wt = Weight percent (%)

A_0 = Weight of initial adsorbent (g)

Example: Amount of Ni^{2+} loading on NaY zeolite (solution : adsorbent = 200)

Result data from AAS (C_{Ni1}) = 2.14 μg/ml

Times of dilution (T) = 25

Therefore, concentration before dilution (C_{Ni2}) = 2.14 * 25

= 53.5 μg/ml

Initial volume of metal solution (V_0) = 100 ml

So, amount of metal loading on NaY zeolite = $53.5 * 100 * 10^{-6}$

= 0.00535 g

Weight of initial adsorbent (A_0) = 0.0955 g

Weight percent (%Wt) $= \frac{0.00535}{0.0955} \times 100$

$= 5.38\ \%$

A1.2 Ion-exchange isotherm

$$E_{A(S)} = \frac{z_A n_{A(S)}}{\Sigma_i z_i n_{i(S)}}$$

(A1.1.2) $$E_A = \frac{z_A n_A}{\Sigma_i z_i n_i}$$

(A1.1.3)

Where,

$E_{A(S)}$ = Equivalent fraction of the cations present within the solution phase

E_A = Equivalent fraction of the cations present within the zeolite

z_A, z_i = Valencies of exchanging cations A and i

$n_{A(S)}$, $n_{i(S)}$ = Moles per unit volume of A and i within solution phase (mmol/ml)

n_A, n_i = Moles per unit volume of A and i within zeolite (mmol/ml)

Example: Amount of $E_{A(S)}$ of NiY zeolite (solution : adsorbent = 200)

In solution,

Ni^{2+}: Result data from AAS = 2.38 μg/ml

Times of dilution = 100

Therefore, concentration before dilution = 2.38 * 100

= 238 μg/ml

Moles per unit volume of Ni^{2+} within zeolite (n_{Ni}) = 0.00405 mmol/ml

Valencies of Ni^{2+} (z_{Ni}) = +2

Thus, $z_{Ni} * n_{Ni}$ = 0.00405 * 2 = 0.0081 mmol/ml

Na^+: Result data from AAS (n_{Na}) = 0.2 μg/ml

Times of dilution = 2500

Therefore, concentration before dilution = 0.2 * 2500

= 500 μg/ml

Moles per unit volume of Ni^{2+} within zeolite (n_{Na}) = 0.02175 mmol/ml

Valencies of Na^{2+} (z_{Na}) = +1

Thus, $z_{Na} * n_{Na}$ = 0.02175 * 1 = 0.02175 mmol/ml

$$\text{So,} \quad E_{Ni(S)} = \frac{0.0081}{0.0081 + 0.02175} = 0.2716$$

In zeolite,

Ni^{2+}: Result data from AAS = 2.14 μg/ml

Times of dilution = 25

Therefore, concentration before dilution = 2.14 * 25

= 53.5 μg/ml

Moles per unit volume of Ni^{2+} within zeolite (n_{Ni}) = 0.00091 mmol/ml

Valencies of Ni^{2+} (z_{Ni}) = +2

Thus, $z_{Ni} * n_{Ni}$ = 0.00091 * 2 = 0.00182 mmol/ml

Na^+: Result data from AAS (n_{Na}) = 0.31 μg/ml

Times of dilution = 100

Therefore, concentration before dilution = 0.31 * 100

= 31 μg/ml

Moles per unit volume of Ni^{2+} within zeolite (n_{Na}) = 0.00135 mmol/ml

Valencies of Na^{2+} (z_{Na}) = +1

Thus, $z_{Na} * n_{Na}$ = 0.00135 * 1 = 0.00135 mmol/ml

$$\text{So,}\quad E_{Ni} = \frac{0.00182}{0.00182 + 0.00135} = 0.5748$$

A2 Calculation of Sulfur Concentration

A2.1 Calibration of Sulfur Compounds

From

$$n_i * RMR_i = A_i$$

$$n_{std} * RMR_{std} = A_{std}$$

$$\text{So,}\quad RMR_i = \frac{A_i * n_{std}(RMR_{std})}{A_{std} * n_i}$$

(A2.1.1)

A2.2 Concentration of Sulfur Compounds in Simulated Fuels

$$Y_i = \frac{A_i / RMR_i}{\sum_{i=1}^{n}\left[A_i / RMR_i\right]}$$

(A2.1.2)

A_i = Peak area of component *i*

n_i = Concentration of component *i* (weight basis)

A_{std} = Peak area of standard component

n_{std} = Concentration of standard component (weight basis)

RMR_i = Respond factor of component *i*

RMR_{std} = Respond factor of standard component

Y_i = Concentration of component *i* from calibration

Respond factor of component *i* (RMR_i)

RMR of 3-methylthiophene = 0.6522

RMR of benzothiophene = 0.6735

RMR of dibenzothiophene = 0.8377

Respond factor of standard component (RMR_{std})

RMR of isooctane = 1

RMR of decane = 1

Example: Adsorption of 3-methylthiophene in isooctane on CuY zeolite (solution : adsorbent = 200) at room temperature

Initial concentration

Peak area of 3-MT1 ($A_{3\text{-}MT(1)}$) = 65656

Peak area of 3-MT2 ($A_{3\text{-}MT(2)}$) = 63705

Peak area of isooctane1 ($A_{std(1)}$) = 61622244

Peak area of isooctane2 ($A_{std(2)}$) = 59126495

$$Y_{3\text{-}MT(1)} = \frac{(65656/0.6522)}{(65656/0.6522)+(61622244/1)}$$

$$= 0.001630875 * 10^6$$

$$= 1630.875 \text{ ppmw}$$

$$Y_{3\text{-}MT(2)} = \frac{(63705/0.6522)}{(63705/0.6522)+(59126495/1)}$$

$$= 0.001649176 * 10^6$$

$$= 1649.176 \text{ ppmw}$$

So, average initial concentration of 3-MT in isooctane

$$Y_{3\text{-}MT} = \frac{1630.875+1649.176}{2}$$

$$= 1640.026 \text{ ppmw}$$

Concentration of 3-MT after adsorption for 8 hours

Peak area of 3-MT1 ($A1_{3\text{-}MT}$) = 21257

Peak area of 3-MT2 ($A2_{3\text{-}MT}$) = 21063

Peak area of isooctane1 ($A1_{std}$) = 63776043

Peak area of isooctane1 ($A2_{std}$) = 64377837

$$
\begin{aligned}
Y_{3\text{-MT}(1)} &= \frac{(21257/0.6522)}{(21257/0.6522)+(63776043/1)} \\
&= 0.000510758 * 10^6 \\
&= 510.758 \text{ ppmw} \\
Y_{3\text{-MT}(2)} &= \frac{(21063/0.6522)}{(21063/0.6522)+(64377837/1)} \\
&= 0.000501370 * 10^6 \\
&= 501.370 \text{ ppmw}
\end{aligned}
$$

So, average concentration of 3-MT in isooctane after adsorption

$$
\begin{aligned}
Y_{3\text{-MT}} &= \frac{510.758+501.370}{2} \\
&= 506.064 \text{ ppmw}
\end{aligned}
$$

A2.3 Calculation of amount of adsorption of sulfur compounds on ion-exchanged zeolite

$$
A_i = \frac{F * C_{ii}}{100} - \left[\frac{C_{if}}{100} * \frac{F * (100 - C_{ii})}{(100 - C_{if})}\right]
$$

A_i = Amount of sulfur compound adsorbed on adsorbent

C_i = Concentration of sulfur compound before adsorption (%)

C_f = Concentration of sulfur compound after adsorption (%)

F = Amount of simulated fuels before adsorption (g)

Example: Adsorption of 3-methylthiophene in isooctane on CuY zeolite (solution : adsorbent = 200) at room temperature

Initial concentration of 3-MT ($C_{3\text{-MTi}}$) = 1640.026 ppmw

$$= 1640.026 * \frac{100}{1000000}$$

$$= 0.164\ \%$$

Concentration of 3-MT after adsorption ($C_{3\text{-}MTf}$) = 506.064 ppmw

$$= 506.064 * \frac{100}{1000000}$$

$$= 0.0506\ \%$$

Amount of simulated fuel = 15.004 g

$$\text{Thus, } A_{3\text{-}MT} = \frac{15.004 * 0.164}{100} - [\frac{0.0506}{100} * \frac{15.004 * (100 - 0.164)}{(100 - 0.0506)}]$$

$$= 0.0189 \text{ g}$$

Molecular weight of 3-MT = 98.1624 g/gmol

$$A_{3\text{-}MT} = \frac{0.0189}{98.1624} * 1000$$

$$= 0.1928 \text{ mmol}$$

Amount of adsorbent (CuY) = 0.177 g

Therefore, the amount of 3-methylthiophene adsorbed on CuY zeolite = $\frac{0.1928}{0.177}$

= 1.0948 mmol/g-sorbent

APPENDIX B Experimental data

Table B1 Amount of metal loading on NaY zeolite with different solution : adsorbent (S/A) in exchanging process

Adsorbent	Concentration of Ni^{2+} in zeolite (μg/ml)	Times of dilution (times)	Concentration before dilution (μg/ml)	Amount of Ni^{2+} (g)	Amount of sorbent (g)	%Wt
NiY (S/A=50)	0.95	25	23.75	0.002375	0.1007	2.36
NiY (S/A=100)	1.81	25	45.25	0.004525	0.1004	4.51
NiY (S/A=200)	2.14	25	53.50	0.00535	0.0995	5.38

Adsorbent	Concentration of Cu^{2+} in zeolite (μg/ml)	Times of dilution (times)	Concentration before dilution (μg/ml)	Amount ofCu^{2+} (g)	Amount of sorbent (g)	%Wt
CuY (S/A=50)	1.14	25	28.50	0.00285	0.1007	2.83
CuY(S/A=100)	2.08	25	52.00	0.0052	0.1004	5.18
CuY(S/A=200)	2.68	25	67.00	0.0067	0.0995	6.73

Table B2 ion-exchange isotherm

Adsorbent	Metal	Valencies of cation (Z_i)	Concentration of metal in zeolite (n_i) (mmol/ml)	Concentration of metal in solution phase ($n_{i(S)}$) (mmol/ml)	E_A	$E_{A(S)}$
NiY (S/A=50)	Ni^{2+}	+2	0.00040	0.00011	0.249	0.011
	Na^+	+1	0.00244	0.01740		
NiY (S/A=100)	Ni^{2+}	+2	0.00077	0.00118	0.441	0.120
	Na^+	+1	0.00196	0.02066		
NiY (S/A=200)	Ni^{2+}	+2	0.00091	0.00405	0.575	0.272
	Na^+	+1	0.00135	0.02175		

Adsorbent	Metal	Valencies of cation (Z_i)	Concentration of metal in zeolite (n_i) (mmol/ml)	Concentration of metal in solution phase ($n_{i(S)}$) (mmol/ml)	E_A	$E_{A(S)}$
CuY (S/A=50)	Cu^{2+}	+2	0.00045	0.00008	0.233	0.010
	Na^+	+1	0.00296	0.01522		
CuY (S/A=100)	Cu^{2+}	+2	0.00082	0.00066	0.491	0.092
	Na^+	+1	0.00170	0.01305		
CuY (S/A=200)	Cu^{2+}	+2	0.00105	0.00348	0.567	0.615
	Na^+	+1	0.00161	0.00435		

Table B3 Adsorption isotherm of 3-methylthiophene in isooctane at room temperature by using NiY zeolite with different solution : adsorbent (S/A) in exchanging process (fuel:adsorbent = 85)

Adsorbent	Initial concentration (ppmw)	$\%C_i$	Final concentration (ppmw)	$\%C_f$	Equilibrium concentration (mmol-S/g-fuel)	Solution weight (g)	Adsorbent weight (g)	Adsorbed 3-MT (mmol-S/g-sorbent)
NiY (S/A=50)	2081.26	0.208	1375.57	0.138	14.0132	15.0037	0.177	0.6102
	1693.39	0.169	1108.86	0.111	11.2962	15.0040	0.177	0.5053
	1448.91	0.145	917.55	0.092	9.3473	15.0022	0.1772	0.4587
	1173.11	0.117	655.86	0.066	6.6814	15.0011	0.1767	0.4476
	770.77	0.077	444.62	0.044	4.5294	15.0023	0.1763	0.2829
NiY (S/A=100)	2081.26	0.208	1258.63	0.126	12.8219	15.0051	0.176	0.7154
	1693.39	0.169	1104.71	0.110	11.2539	15.0040	0.177	0.5089
	1448.91	0.145	895.30	0.090	9.1206	15.0041	0.1772	0.4780
	1173.11	0.117	657.92	0.066	6.7024	15.0077	0.1771	0.4450
	770.77	0.077	404.64	0.040	4.1221	15.0014	0.1763	0.3175
NiY (S/A=200)	2081.26	0.208	1354.27	0.135	13.7962	15.0070	0.1763	0.6313
	1693.39	0.169	1123.22	0.112	11.4424	15.0040	0.1766	0.4940
	1448.91	0.145	913.94	0.091	9.3105	15.0032	0.1771	0.4621
	1173.11	0.117	688.72	0.069	7.0162	15.0014	0.1763	0.4202
	770.77	0.077	476.49	0.048	4.8541	15.0029	0.177	0.2542
NaY	2051.67	0.205	1308.86	0.131	13.3337	15.0032	0.1767	0.6434
	1684.40	0.168	1062.56	0.106	10.8245	15.0030	0.1767	0.5384
	1400.91	0.140	787.18	0.079	8.0192	15.0030	0.1764	0.5322
	1082.60	0.108	579.23	0.058	5.9007	15.0100	0.1766	0.4361
	781.38	0.078	428.11	0.043	4.3612	15.0100	0.1766	0.3060

Table B4 Adsorption isotherm of benzothiophene in isooctane at room temperature by using NiY zeolite with different solution : adsorbent (S/A) in exchanging process (fuel:adsorbent = 85)

Adsorbent	Initial concentration (ppmw)	%C_i	Final concentration (ppmw)	%C_f	Equilibrium concentration (µmol-S/g-fuel)	Solution weight (g)	Adsorbent weight (g)	Adsorbed BT (mmol-S/g-sorbent)
NiY (S/A=50)	2024.31	0.202	593.00	0.059	4.4189	15.0020	0.1767	0.9061
	1736.61	0.174	435.96	0.044	3.2487	15.0057	0.1769	0.8225
	1453.07	0.145	325.05	0.033	2.4222	15.0042	0.1766	0.7144
	1095.66	0.110	187.57	0.019	1.3977	15.0004	0.1768	0.5742
	784.95	0.078	74.30	0.007	0.5537	15.0052	0.1761	0.4513
NiY (S/A=100)	2024.31	0.202	584.11	0.058	4.3527	15.0037	0.1772	0.9092
	1736.61	0.174	405.73	0.041	3.0234	15.0012	0.1768	0.8418
	1453.07	0.145	399.26	0.040	2.9752	15.0076	0.1757	0.6710
	1095.66	0.110	163.36	0.016	1.2173	15.0048	0.1765	0.5907
	784.95	0.078	116.06	0.012	0.8649	15.0047	0.1773	0.4219
NiY (S/A=200)	2024.31	0.202	560.10	0.056	4.1738	15.0024	0.1763	0.9290
	1736.61	0.174	440.21	0.044	3.2803	15.0062	0.1770	0.8194
	1453.07	0.145	295.10	0.030	2.1990	15.0068	0.1770	0.7318
	1095.66	0.110	180.97	0.018	1.3486	15.0066	0.1768	0.5786
	784.95	0.078	80.18	0.008	0.5975	15.0004	0.1760	0.4476
NaY	1976.54	0.198	642.82	0.064	4.7902	15.0080	0.1767	0.8447
	1798.56	0.180	474.65	0.047	3.5370	15.0020	0.1768	0.8375
	1351.52	0.135	290.50	0.029	2.1648	15.0080	0.1765	0.6725
	1075.16	0.108	162.50	0.016	1.2109	15.0027	0.1768	0.5772
	805.08	0.081	70.70	0.007	0.5268	15.0060	0.1760	0.4666

Table B5 Adsorption isotherm of dibenzothiophene in decane at room temperature by using NiY zeolite with different solution : adsorbent (S/A) in exchanging process (fuel:adsorbent = 85)

Adsorbent	Initial concentration (ppmw)	%C_i	Final concentration (ppmw)	%C_f	Equilibrium concentration (µmol-S/g-fuel)	Solution weight (g)	Adsorbent weight (g)	Adsorbed DBT (mmol-S/g-sorbent)
NiY (S/A=50)	1877.44	0.188	221.43	0.022	1.2017	15.0062	0.1762	0.7656
	1786.32	0.179	152.11	0.015	0.8255	15.0010	0.1770	0.7518
	1352.74	0.135	81.77	0.008	0.4438	15.0030	0.1765	0.5864
	1135.49	0.114	71.51	0.007	0.3881	15.0062	0.1763	0.4915
	792.30	0.079	18.20	0.002	0.0988	15.0043	0.1761	0.3580
NiY (S/A=100)	1877.44	0.188	239.93	0.024	1.3022	15.0010	0.1755	0.7598
	1786.32	0.179	307.57	0.031	1.6692	15.0046	0.1768	0.6813
	1352.74	0.135	65.14	0.007	0.3535	15.0029	0.1765	0.5940
	1135.49	0.114	55.81	0.006	0.3029	15.0041	0.1762	0.4990
	792.30	0.079	16.85	0.002	0.0915	15.0071	0.1764	0.3580
NiY (S/A=200)	1877.44	0.188	317.66	0.032	1.7240	15.0000	0.1760	0.7217
	1786.32	0.179	253.48	0.025	1.3757	15.0024	0.1770	0.7053
	1352.74	0.135	106.02	0.011	0.5754	15.0008	0.1770	0.5735
	1135.49	0.114	57.68	0.006	0.3131	15.0016	0.1762	0.4981
	792.30	0.079	19.34	0.002	0.1049	15.0028	0.1766	0.3564
NaY	1877.44	0.188	232.26	0.023	1.2606	15.0049	0.1760	0.7614
	1688.12	0.169	161.24	0.016	0.8751	15.0025	0.1765	0.7045
	1405.50	0.141	80.97	0.008	0.4394	15.0027	0.1763	0.6118
	1135.49	0.114	53.89	0.005	0.2925	15.0030	0.1762	0.4999
	792.30	0.079	33.42	0.003	0.1814	15.0003	0.1771	0.3489

Table B6 Adsorption isotherm of 3-methylthiophene in isooctane at room temperature by using CuY zeolite with different solution : adsorbent (S/A) in exchanging process (fuel:adsorbent = 85)

Adsorbent	Initial concentration (ppmw)	%C_i	Final concentration (ppmw)	%C_f	Equilibrium concentration (mmol-S/g-fuel)	Solution weight (g)	Adsorbent weight (g)	Adsorbed 3-MT (mmol-S/g-sorbent)
CuY (S/A=50)	1967.62	0.197	1145.00	0.115	11.6643	15.0013	0.1771	0.6102
	1640.03	0.164	752.15	0.075	7.6623	15.0045	0.1765	0.5053
	1398.42	0.140	719.77	0.072	7.3324	15.0020	0.1769	0.4587
	1076.97	0.108	514.87	0.051	5.2451	15.0080	0.1765	0.4476
	825.37	0.083	369.61	0.037	3.7653	15.0043	0.1771	0.2829
CuY (S/A=100)	1967.62	0.197	917.79	0.092	9.3497	15.0065	0.1768	0.7154
	1640.03	0.164	678.83	0.068	6.9154	15.0026	0.1770	0.5089
	1398.42	0.140	602.74	0.060	6.1402	15.0015	0.1762	0.4780
	1076.97	0.108	359.13	0.036	3.6586	15.0020	0.1760	0.4450
	825.37	0.083	249.67	0.025	2.5434	15.0062	0.1767	0.3175
CuY (S/A=200)	1967.62	0.197	707.25	0.071	7.2049	15.0048	0.1761	0.6313
	1640.03	0.164	515.51	0.052	5.2516	15.0040	0.1770	0.4940
	1398.42	0.140	340.21	0.034	3.4658	15.0022	0.1767	0.4621
	1076.97	0.108	304.31	0.030	3.1001	15.0053	0.1771	0.4202
	825.37	0.083	150.05	0.015	1.5286	15.0051	0.1760	0.2542
NaY	2051.55	0.205	1308.78	0.131	13.3328	15.0032	0.1767	0.6434
	1684.29	0.168	1062.49	0.106	10.8238	15.0030	0.1767	0.5384
	1400.82	0.140	787.13	0.079	8.0187	15.0030	0.1764	0.5322
	1082.54	0.108	579.19	0.058	5.9004	15.0100	0.1766	0.4361
	781.33	0.078	428.08	0.043	4.3609	15.0100	0.1766	0.3060

Table B7 Adsorption isotherm of benzothiophene in isooctane at room temperature by using CuY zeolite with different solution : adsorbent (S/A) in exchanging process (fuel:adsorbent = 85)

Adsorbent	Initial concentration (ppmw)	%C_i	Final concentration (ppmw)	%C_f	Equilibrium concentration (µmol-S/g-fuel)	Solution weight (g)	Adsorbent weight (g)	Adsorbed BT (mmol-S/g-sorbent)
CuY (S/A=50)	1968.14	0.197	622.00	0.062	4.6350	15.0070	0.1763	0.8544
	1723.24	0.172	415.07	0.042	3.0930	15.0045	0.1761	0.8309
	1387.30	0.139	222.79	0.022	1.6602	15.0036	0.1771	0.7353
	1227.88	0.123	158.37	0.016	1.1801	15.0040	0.1770	0.6757
	679.42	0.068	76.55	0.008	0.5705	15.0043	0.1771	0.3806
CuY (S/A=100)	1968.14	0.197	548.40	0.055	4.0866	15.0040	0.1765	0.8999
	1723.24	0.172	322.43	0.032	2.4027	15.0050	0.1770	0.8852
	1387.30	0.139	151.00	0.015	1.1252	15.0067	0.1762	0.7848
	1227.88	0.123	65.55	0.007	0.4885	15.0064	0.1767	0.7356
	679.42	0.068	14.81	0.001	0.1104	15.0062	0.1767	0.4206
CuY (S/A=200)	1968.14	0.197	438.53	0.044	3.2679	15.0030	0.1767	0.9682
	1723.24	0.172	264.72	0.026	1.9726	15.0025	0.1770	0.9215
	1387.30	0.139	75.82	0.008	0.5650	15.0038	0.1767	0.8299
	1227.88	0.123	65.55	0.007	0.4885	15.0058	0.1770	0.7344
	679.42	0.068	8.02	0.001	0.0598	15.0051	0.1760	0.4266
NaY	1976.54	0.198	642.82	0.064	4.7902	15.0080	0.1767	0.8447
	1798.56	0.180	474.65	0.047	3.5370	15.0020	0.1768	0.8375
	1351.52	0.135	290.50	0.029	2.1648	15.0080	0.1765	0.6725
	1075.16	0.108	162.50	0.016	1.2109	15.0027	0.1768	0.5772
	805.08	0.081	70.70	0.007	0.5268	15.0060	0.1760	0.4666

Table B8 Adsorption isotherm of dibenzothiophene in decane at room temperature by using CuY zeolite with different solution : adsorbent (S/A) in exchanging process (fuel:adsorbent = 85)

Adsorbent	Initial concentration (ppmw)	%C_i	Final concentration (ppmw)	%C_f	Equilibrium concentration (μmol-S/g-fuel)	Solution weight (g)	Adsorbent weight (g)	Adsorbed DBT (mmol-S/g-sorbent)
CuY (S/A=50)	1983.83	0.198	300.30	0.030	1.6298	15.0079	0.1767	0.7763
	1616.89	0.162	117.04	0.012	0.6352	15.0070	0.1763	0.6930
	1423.10	0.142	66.95	0.007	0.3633	15.0046	0.1767	0.6250
	1147.24	0.115	42.94	0.004	0.2330	15.0030	0.1768	0.5086
	855.70	0.086	28.61	0.003	0.1553	15.0043	0.1771	0.3803
CuY (S/A=100)	1983.83	0.198	255.60	0.026	1.3872	15.0005	0.1771	0.7947
	1616.89	0.162	107.17	0.011	0.5816	15.0000	0.1769	0.6948
	1423.10	0.142	26.10	0.003	0.1416	15.0027	0.1770	0.6427
	1147.24	0.115	19.95	0.002	0.1083	15.0065	0.1767	0.5196
	855.70	0.086	25.19	0.003	0.1367	15.0062	0.1767	0.3828
CuY (S/A=200)	1983.83	0.198	224.50	0.022	1.2184	15.0064	0.1770	0.8097
	1616.89	0.162	62.94	0.006	0.3416	15.0003	0.1770	0.7148
	1423.10	0.142	25.96	0.003	0.1409	15.0078	0.1770	0.6429
	1147.24	0.115	20.53	0.002	0.1114	15.0012	0.1767	0.5191
	855.70	0.086	20.31	0.002	0.1102	15.0051	0.1760	0.3865
NaY	1877.44	0.188	232.26	0.023	1.2606	15.0049	0.1760	0.7614
	1688.12	0.169	161.24	0.016	0.8751	15.0025	0.1765	0.7045
	1405.50	0.141	80.97	0.008	0.4394	15.0027	0.1763	0.6118
	1135.49	0.114	53.89	0.005	0.2925	15.0030	0.1762	0.4999
	792.30	0.079	33.42	0.003	0.1814	15.0003	0.1771	0.3489

APPENDIX C Simulation Program for FORTRAN

C1 FORTRAN PROGRAM

```
program Peng_Robinson_param_estim
implicit none
integer Nc
parameter (Nc=2)
integer M, N
parameter (M=7, N = 2* ( (Nc**2) - Nc) /2 )
integer LRW , LIW
parameter (LRW = max( (3*N*N+M*N+2*M+6*N) ,
    &  (2*N+105+N*(M+2*N+21)+2*M))
    &  ,LIW = 82+4*N)
integer I_opt(14) , I_print(10) , num_optim , ideriv , lp
    &  , ier , iw(LIW)
double precision R_opt(18) ,eps_f , ssq ! pour utiliser min_somme_carres
    &  , RW(LRW)
double precision XGUESS(N),X(N), XLB(N), XSCALE(N), XUB(N)
integer i,j,i_X
doubleprecision k_ij(Nc,Nc),l_ij(Nc,Nc)
doubleprecision T_c(Nc),P_c(Nc),w(Nc) ! supercritical phase parameters
COMMON /SC_param/ T_c,P_c,w
EXTERNAL Calc_SCE

!          Sc phase parameters
           T_c(1) = 579.4d0
           P_c(1) = 56.16979d0
           w(1) = 3.84d-1
           T_c(2) = 304.d0
           P_c(2) = 77.d0
           w(2) = 2.28d-1
```

```
!       Initialisation of the parameters
        k_ij(1,2) = 1.d0
        l_ij(1,2) = 1.d0

!       Use of the minimization subroutine
        i_X = 0
        Do i=1,(Nc-1)
                Do j=i+1,Nc
                        i_X = i_X + 1
                        XGUESS(i_X) = k_ij(i,j)
                        XGUESS(i_X + ((Nc**2) - Nc) /2) = l_ij(i,j)
                EndDo !j=i+1,Nc
        EndDo !i=1,(Nc-1)

!       Uper and Lower bonds of the parameters
        Do i = 1, N
                XLB(i) = 1.d-10
                XUB(i) = 1.d0
        EndDo !i = 1, N

!       Precision parameter
        eps_f = 1.d-6

        Do i = 1, N
                XSCALE(i) = 1.d0
        EndDo !i = 1, N

        i_opt(1) = 0
        i_print(1) = 0
        ideriv = 0
```

```
!!!!!! TWARS2
X=XGUESS
num_optim = 2 ! 1: DBCLSF  2: TWARS2  3: DN2FB
CALL min_somme_carres ( Calc_SCE, X, N, M
   &                  , XLB , XUB
   &                  , eps_f, XSCALE , num_optim
   &                  , i_opt, r_opt, i_print
   &                  , lp
   &                  , rw, lrw, iw, liw
   &                  , ideriv
   &                  , ssq, ier)
Write(*,*) X
Write(*,*) SSQ
END
!***************************************************************
        SUBROUTINE calc_jcb_ssq (nob, np, param, dR_dP, ld_dR_dP)
        END

Subroutine Calc_SCE (M, N, X, F)
implicit none
integer Nc
parameter (Nc=2)
integer M ! M : nb of point for the estimation
integer N ! N : nb of parameter to estimate
integer i,j,i_X
doubleprecision X(N),F(M)
doubleprecision k_ij(Nc,Nc),l_ij(Nc,Nc) ! supercritical phase parameters
doubleprecision T,Y(Nc),V(M) ! state of the supercritical phase: temperature and
                                        composition
doubleprecision P_exp(M),P_cal(M)
doubleprecision T_c(Nc),P_c(Nc),w(Nc) ! supercritical phase parameters
COMMON /SC_param/ T_c,P_c,w
```

```
        i_X = 0
        Do i=1,(Nc-1)
                k_ij(i,i) = 0.d0
                l_ij(i,i) = 0.d0

                Do j=i+1,Nc
                        i_X = i_X + 1

                        k_ij(i,j)=X(i_X)
                        k_ij(j,i)=X(i_X)

                        l_ij(i,j)=X(i_X + ((Nc**2) - Nc) /2)
                        l_ij(j,i)=X(i_X + ((Nc**2) - Nc) /2)
                EndDo !j=i+1,Nc
        EndDo !i=1,(Nc-1)
        k_ij(Nc,Nc) = 0.d0
        l_ij(Nc,Nc) = 0.d0
OPEN (11,FILE='Thiophene.xls',STATUS='OLD')
Do i=1,M
        READ(11,*) T,P_exp,Y(1)
        Y(2)=1.d0-Y(1)
        V(i) = (0.0004*(P_exp(i)**2.d0))-(0.0561*P_exp(i))+2.1151 ! molar volume
function of P and T

Call Mixture_PR(P_cal(i),T,k_ij,l_ij,Y,V(i))

        F(i) = (P_exp(i)-P_cal(i))/P_exp(i)
EndDo !i=1,M

CLOSE(11)
END
```

```
Subroutine Mixture_PR(P,T,k_ij,l_ij,Y,V)
implicit none
integer Nc,M
parameter (Nc=2,M=7)
doubleprecision R
parameter (R=8.314d0)
doubleprecision P,T,V,Y(Nc)
doubleprecision k_ij(Nc,Nc),l_ij(Nc,Nc)
doubleprecision Gam(Nc),a_ij(Nc,Nc),b_ij(Nc,Nc),a_m,b_m
integer i,j
doubleprecision T_c(Nc),P_c(Nc),w(Nc) ! supercritical phase parameters
COMMON /SC_param/ T_c,P_c,w

Do i=1,Nc
        Gam(i) = (1.d0 + (0.37464d0 +
   &                    (1.54226d0 * w(i)) - (0.26992d0 * (w(i)**2) ) )
   &                    )/(1.d0-SQRT(T/T_c(i)))

        a_ij(i,i) = 0.457235d0 * (R**2) * (T_c(i)**2) * Gam(i) / P_c(i)

        b_ij(i,i) = 0.07779 * R * T_c(i)/P_c(i)
EndDo !i=1,Nc


Do i=1,Nc
        Do j=1,Nc
                If (i.NE.j) Then
                        a_ij(i,j) = (1.d0 - k_ij(i,j) ) *
   &                                    SQRT(a_ij(i,i) * a_ij(j,j))
                        b_ij(i,j) = (1.d0 - l_ij(i,j) ) *
   &                                    ( (b_ij(i,i)**(1.d0/3.d0) )
   &                                    + (b_ij(j,j)**(1.d0/3.d0) )**3) / 8.d0
```

```
                EndIf
        EndDo !j=1,Nc
EndDo !i=1,Nc
a_m = 0.d0
b_m = 0.d0
Do i=1,Nc
        Do j=1,Nc
                a_m = a_m + Y(i) * Y(j) * a_ij(i,j)
                b_m = b_m + Y(i) * Y(j) * b_ij(i,j)
        EndDo !j=1,Nc
EndDo !i=1,Nc

Do i=1,M
        P = ( (R*T)/(V(i)-b_m) ) -
   &            (a_m / ( (V(i)**2) + 2.d0 * V(i) * b_m - (b_m**2) ) )
EndDo
END
```

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