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## NOTATIONS

A	cross section area of column , $\text{cm}^2$
a	particle surface area in bed , $\text{cm}^2/\text{g}$
$a_i$	activity coefficient of solute i
$C_0$	initial concentration of adsorbable liquid , $\text{mg/ml}$
$C_a$	equilibrium concentration of adsorbable liquid in bulk liquid, $\text{mg/ml}$
$\bar{C}$	concentration of adsorbable liquid in bulk phase , $\text{mg/ml}$
$C^*$	concentration of adsorbable liquid in equilibrium with q , $\text{mg/ml}$
C	concentration of adsorbable liquid in the void space , $\text{mg/ml}$
$C_i$	concentration of adsorbable liquid at adsorbent interface , $\text{mg/ml}$
$D_1$	axial dispersion coefficient , $\text{cm}^2/\text{min}$
$D_s$	surface diffusion coefficient , $\text{cm}^2/\text{min}$
$D_v$	liquid diffusivity , $\text{cm}^2/\text{sec}$
E	$(C_0 - C) / (C_0 - C_a)$
g	amount of adsorbent , g
Kc	overall mass transfer coefficient , $\text{cm}/\text{min}$
kf	external fluid film mass transfer coefficient , $\text{cm}/\text{min}$
$k_{int}$	internal mass transfer coefficient , $\text{cm}/\text{min}$
$M_s$	molecular weight of solvent
m	space index within column
$N_r$	diffusion flux in adsorbent particle
$N_c$	diffusion flux in column
$N_{Pe}$	Peclet number = $U D / D_1$

$N_{Re}$	Reynolds number = $D_p U_o \rho / \mu$
$N_{Sc}$	Schmidt number = $\mu / \rho D_v$
$N_{Sh}$	Sherwood number = $k_f D / D_v$
$n$	time index
$n^o$	total moles in solution, mmole
$n_s^o$	surface excess, mmol/g adsorbent
$n'$	moles of solute in adsorbed phase, mmole
$P$	pressure
$q$	amount adsorbed at point $r$ , mg/g
$\bar{q}$	average amount adsorbed, mg/g
$R$	gas constant
$R_p$	particle radius, cm
$r$	radius position within the particle, cm
$T$	absolute temperature, K
$t$	time, min
$U_o$	superficial liquid velocity, cm/min
$V$	volume adsorbed
$V_A$	molar volume of solute as liquid at its normal boiling point, $cm^3/g \text{ mol}$
$V_b$	volume of bulk liquid in bed, ml
$V_p$	volume of pore in adsorbent, ml
$V_s$	volume of solid adsorbent, ml
$v$	volume of given cut
$x_i^o$	initial mole fraction of solute $i$
$x_i'$	mole fraction of $i$ in adsorbed phase
$x_i$	equilibrium mole fraction of solute $i$
$Z$	column length, cm
$\rho_b$	bed density, $g/cm^3$

$\rho_p$	particle density , g/cm <sup>3</sup>
$\epsilon$	void fraction in bed
$\gamma$	excess number of moles of solute in solution
$\theta$	dimensionless time , $\frac{D_p \cdot t}{r^2}$
$\mu$	viscosity of solution , cP
$\psi_s$	association parameter for solvent
$\delta$	surface tension of the solution
$\beta$	constant in Freundlich isotherm

**APPENDICES**

## APPENDIX A

## BREAKTHROUGH CURVES DATA

TABLE A1

The output concentration of n-hexane passing through the packed column (velocity 1.59 cm/min,  $C_0 = 150.27$  mg/ml, bed length 46.00cm) at 15 C .

Time(min)	C(mg/ml)	C/ $C_0$
1.00	0.0000	0.0000
2.00	0.0000	0.0000
3.00	0.0000	0.0000
4.00	0.0000	0.0000
5.00	0.0000	0.0000
6.00	0.0000	0.0000
7.00	0.0000	0.0000
8.00	0.0000	0.0000
9.00	0.0000	0.0000
10.00	0.0000	0.0000
11.00	0.0000	0.0000
12.00	0.0000	0.0000
13.00	0.0000	0.0000
14.00	3.7570	0.0250
15.00	7.5130	0.0500
16.00	16.5290	0.1100



17.00	31.5560	0.2100
18.00	43.5780	0.2900
19.00	60.1080	0.4000
20.00	78.1400	0.5200
21.00	105.1890	0.7000
22.00	114.2050	0.7600
23.00	118.7133	0.7900
24.00	121.7180	0.8100
25.00	124.7240	0.8300
26.00	129.2320	0.8600
27.00	129.2320	0.8600
28.00	132.2370	0.8800
29.00	133.7400	0.8900
30.00	133.7400	0.8900

TABLE A2

The output concentration of n-hexane passing through the packed column (velocity 1.53 cm/min,  $C_0 = 238.32$  mg/ml, bed length 44.50 cm) at 15 C .

Time(min)	C(mg/ml)	C/ $C_0$
1.00	0.0000	0.0000
2.00	0.0000	0.0000
3.00	0.0000	0.0000
4.00	0.0000	0.0000
5.00	0.0000	0.0000

6.00	0.0000	0.0000
7.00	0.0000	0.0000
8.00	0.0000	0.0000
9.00	0.0000	0.0000
10.00	0.0000	0.0000
11.00	0.0000	0.0000
12.00	0.0000	0.0000
13.00	0.0000	0.0000
14.00	11.9160	0.0500
15.00	19.0650	0.0800
16.00	30.9800	0.1300
17.00	59.5800	0.2500
18.00	97.7110	0.4100
19.00	133.4590	0.5600
20.00	171.5900	0.7200
21.00	193.0390	0.8100
22.00	204.9550	0.8600
23.00	209.7216	0.8800
24.00	216.8720	0.9100
25.00	214.4880	0.9000
26.00	226.4040	0.9500
27.00	226.4040	0.9500
28.00	226.4040	0.9500
29.00	226.4040	0.9500
30.00	228.7870	0.9600

TABLE A3

The output concentration of n-hexane passing through the packed column (velocity 2.90 cm/min,  $C_0 = 332.98$  mg/ml, bed length 46.50 cm) at 15 C .

Time(min)	C(mg/ml)	C/ $C_0$
1.00	0.0000	0.0000
2.00	0.0000	0.0000
3.00	0.0000	0.0000
4.00	0.0000	0.0000
5.00	0.0000	0.0000
6.00	0.0000	0.0000
7.00	0.0000	0.0000
8.00	16.6490	0.0500
9.00	53.2760	0.1600
10.00	169.8190	0.5100
11.00	243.0750	0.7300
12.00	286.3620	0.8600
13.00	306.3400	0.9200
14.00	316.3310	0.9500
15.00	319.6600	0.9600
16.00	319.6600	0.9600
17.00	322.9900	0.9700
18.00	322.9900	0.9700
19.00	322.9900	0.9700
20.00	326.3200	0.9800
21.00	322.9900	0.9700

22.00	322.9900	0.9700
23.00	326.3200	0.9800
24.00	319.6600	0.9600
25.00	326.3200	0.9800

TABLE A4

The output concentration of n-hexene passing through the packed column (velocity 2.94 cm/min,  $C_0 = 157.35$  mg/ml, bed length 45.50cm) at 15 C .

Time(min)	C(mg/ml)	C/ $C_0$
1.00	0.0000	0.0000
2.00	0.0000	0.0000
3.00	0.0000	0.0000
4.00	0.0000	0.0000
5.00	0.0000	0.0000
6.00	0.0000	0.0000
7.00	0.0000	0.0000
8.00	6.2940	0.0400
9.00	25.1760	0.1600
10.00	48.7780	0.3100
11.00	81.8220	0.5200
12.00	108.5715	0.6900
13.00	130.6005	0.8300
14.00	136.8940	0.8700
15.00	144.7620	0.9200

16.00	146.3350	0.9300
17.00	149.4820	0.9500
18.00	149.4820	0.9500
19.00	149.4820	0.9500
20.00	153.4160	0.9750
21.00	151.0560	0.9600
22.00	151.0560	0.9600
23.00	151.0560	0.9600
24.00	151.0560	0.9600
25.00	151.0560	0.9600

TABLE A5

The output concentration of n-hexane passing through the packed column (velocity 3.70 cm/min,  $C_0 = 140.34$  mg/ml, bed length 47.00cm) at 15 C .

Time(min)	C(mg/ml)	C/ $C_0$
1.00	0.0000	0.0000
2.00	0.0000	0.0000
3.00	0.0000	0.0000
4.00	0.0000	0.0000
5.00	0.0000	0.0000
6.00	8.4190	0.0600
7.00	21.0480	0.1500
8.00	64.5470	0.4600
9.00	94.0140	0.6700

10.00	113.6590	0.8100
11.00	123.4810	0.8800
12.00	127.6900	0.9100
13.00	130.4970	0.9300
14.00	131.9000	0.9400
15.00	134.7000	0.9600
16.00	133.3040	0.9500
17.00	136.1100	0.9700
18.00	137.5130	0.9800
19.00	136.1100	0.9700
20.00	138.9160	0.9900
21.00	136.1100	0.9700
22.00	137.5130	0.9800
23.00	137.5130	0.9800
24.00	136.1100	0.9700
25.00	136.1100	0.9700

TABLE A6

The output concentration of n-hexane passing through the packed column (velocity 2.40 cm/min,  $C_0 = 139.21$  mg/ml, bed length 48.00cm) at 15 C .

Time(min)	C(mg/ml)	C/Co
1.00	0.0000	0.0000
2.00	0.0000	0.0000
3.00	0.0000	0.0000

4.00	0.0000	0.0000
5.00	0.0000	0.0000
6.00	0.0000	0.0000
7.00	0.0000	0.0000
8.00	5.5680	0.0400
9.00	6.9600	0.0500
10.00	9.7440	0.0700
11.00	15.3130	0.1100
12.00	43.1550	0.3100
13.00	66.8200	0.4800
14.00	76.5650	0.5500
15.00	101.6230	0.7300
16.00	112.7600	0.8100
17.00	122.5040	0.8800
18.00	125.2890	0.9000
19.00	129.4650	0.9300
20.00	130.8570	0.9400
21.00	132.2490	0.9500
22.00	132.2490	0.9500
23.00	132.2490	0.9500
24.00	133.6410	0.9600
25.00	133.6410	0.9600

## APPENDIX B

## ISOTHERM DATA

The different concentration of n-hexane initially and at equilibrium in mixture of n-hexane and cyclohexane on activated carbon at 15 C are presented in table B1.

TABLE B1

Experimental data at equilibrium.

$x_1$	C (mg/ml)	$n_1^0$ (mmol/g)	q (mg/g)	lnC	lnq
0.0600	39.7200	0.3594	50.7880	3.6819	3.9277
0.0610	40.3820	0.2527	46.1810	3.6984	3.8326
0.9600	63.5520	0.5878	82.2168	4.1519	4.4094
0.1100	72.8200	0.5884	90.2622	4.2880	4.5027
0.1120	74.1440	0.8185	102.5413	4.3060	4.6303
0.1900	125.8700	0.6267	137.6910	4.8345	4.9250
0.1930	127.7660	0.6841	141.9586	4.8502	4.9550
0.2030	134.3860	0.6941	148.4328	4.9007	5.0001
0.2110	139.6820	0.8975	162.4608	4.9394	5.0904
0.2900	191.9800	0.7699	201.7511	5.2574	5.3070
0.2960	195.9520	0.6960	201.3172	5.2779	5.3049
0.2990	197.9380	0.8569	211.2138	5.2880	5.3529
0.3060	202.5720	0.7723	210.5554	5.3111	5.3497



0.3920	259.5040	0.7107	256.9471	5.5588	5.5489
0.4000	264.8000	0.6466	257.7452	5.5790	5.5520
0.4050	268.1100	0.6697	262.3889	5.5941	5.5698
0.4920	325.7040	0.5927	307.9662	5.7860	5.7300
0.4950	327.6900	0.5501	307.4907	5.7921	5.7284
0.5030	332.9860	0.6010	314.3506	5.8081	5.7505
0.5050	334.3100	0.4899	310.1929	5.8121	5.7372
0.5980	392.5660	0.3860	354.4578	5.9727	5.8706
0.5980	395.8760	0.3932	357.8725	5.9811	5.8802
0.6010	397.8620	0.6171	371.2161	5.9861	5.9168
0.6870	454.7940	0.2847	402.6440	6.1198	5.9981
0.6900	456.7800	0.2223	400.9881	6.1242	5.9939
0.7040	466.0480	0.3986	418.1799	6.1443	6.0359
0.7080	468.6960	0.4143	421.4531	6.1500	6.0437
0.7940	525.6280	0.2962	463.8702	6.2646	6.1396
0.8000	529.6000	0.0793	455.5276	6.2721	6.1215
0.8040	532.2480	0.2739	468.2724	6.2771	6.1491
0.8820	583.8840	0.0782	501.7903	6.3697	6.2182
0.8860	586.5320	0.1748	509.3660	6.3742	6.2332
0.8960	593.1520	0.0764	509.5522	6.3855	6.2335
0.8970	593.8140	0.1738	515.5195	6.3866	6.2452
0.9490	628.2380	0.3768	556.1127	6.4429	6.3210

## APPENDIX C

DERIVATION OF THE MATHEMATICAL EXPRESSIONS USED TO  
PREDICT THE BREAKTHROUGH CURVES

With the assumption as shown in chapter 2 the  
concentration  $C(z,t)$  is determined by the following steps.

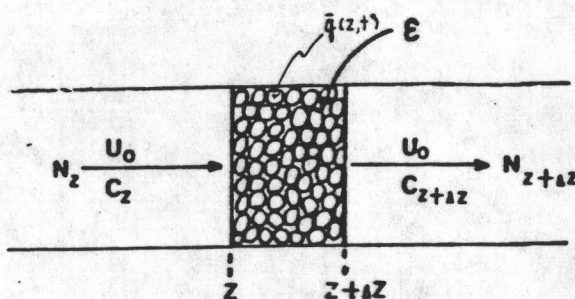


Figure C1 Mass balance in column.

Mass balance in liquid phase ;

$$\begin{aligned}
 & N_z A \Delta t \Big|_z - N_{z+\Delta z} A \Delta t \Big|_{z+\Delta z} + A U \Delta t \bar{C} \Big|_z - A U \Delta t \bar{C} \Big|_{z+\Delta z} + \epsilon A \Delta z \bar{C}(t) - \epsilon A \Delta z \bar{C}(t+\Delta t) \\
 & + (1-\epsilon) \rho_s A \Delta z (\bar{q}(t) - \bar{q}(t+\Delta t)) = 0 \quad (C.1)
 \end{aligned}$$

division by  $A \Delta t \Delta z$  and taking the limit as  $\Delta t \rightarrow 0$  and  $\Delta z \rightarrow 0$  gives

$$\begin{aligned}
 & \frac{N_z - N_{z+\Delta z}}{\Delta z} + \frac{U(\bar{C}_z - \bar{C}_{z+\Delta z})}{\Delta z} + \frac{(\bar{C}(t) - \bar{C}(t+\Delta t))}{\Delta t} + \rho_s (1-\epsilon) \frac{(\bar{q}(t) - \bar{q}(t+\Delta t))}{\Delta t} \\
 & = 0 \quad (C.2)
 \end{aligned}$$

$$-\frac{\partial N}{\partial z} - U\frac{\partial \bar{C}}{\partial z} - \frac{\partial \bar{C}}{\partial t} - (1-\epsilon)_p \frac{\partial \bar{q}}{\partial t} = 0 \quad (\text{C.3})$$

for  $N = -D1 \frac{\partial \bar{C}}{\partial z}$  then

$$-D1 \frac{\partial^2 \bar{C}}{\partial z^2} + U \frac{\partial \bar{C}}{\partial z} + \frac{\partial \bar{C}}{\partial t} + (1-\epsilon)_p \frac{\partial \bar{q}}{\partial t} = 0 \quad (\text{C.4})$$

the rate of adsorption assumed to be linear is expressed as

$$(1-\epsilon)_p \frac{\partial \bar{q}}{\partial t} = Kc.a.(C1-C^2) \quad (\text{C.5})$$

Mass balance in the adsorbent particle :

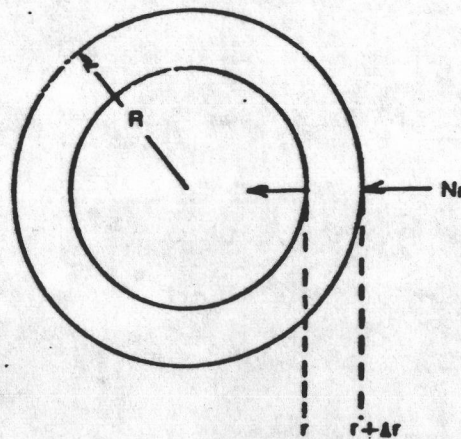


Figure C2 Mass balance in adsorbent particle.

$$N_r \Big|_{r+\Delta r} 4\pi(r+\Delta r)^2 - N_r \Big|_r 4\pi r^2 = 4\pi r^2 \Delta r \frac{\partial q}{\partial t} \quad (\text{C.6})$$

division by  $4\pi r \Delta r$  and taking the limit as  $\Delta r \rightarrow 0$  gives

$$\frac{\partial N_r r^2}{\partial r} = r^2 \frac{\partial q}{\partial t} \quad (\text{C.7})$$

$$\text{for } N_r = -D_s \frac{\partial q}{\partial r}$$

$$\frac{\partial q}{\partial t} = -D_s \left( \frac{\partial^2 q}{\partial r^2} + \frac{2}{r} \frac{\partial q}{\partial r} \right) \quad (\text{C.8})$$

the external diffusion boundary condition may be expressed as

$$D_s \frac{\partial q}{\partial r} \Big|_{r=R} = k_f (\bar{C} - C_s) \quad (\text{C.9})$$

the average solid phase concentration,  $\bar{q}$  is calculated by

$$\bar{q} = \frac{3}{R^3} \int_0^R q r^2 dr \quad (\text{C.10})$$

the internal diffusion boundary condition may be written as

$$\frac{\partial q}{\partial r} = 0 \quad \text{at} \quad r = 0 \quad (\text{C.11})$$

The appropriate boundary and initial conditions for these equations are as follows :

$$\bar{C} = 0 \quad \text{at} \quad t = 0, \quad z \geq 0 \quad (\text{C.12})$$

$$\bar{q} = 0 \quad \text{at} \quad t = 0, \quad z \geq 0 \quad (\text{C.13})$$

$$\bar{C} = C_0 \quad \text{at} \quad t > 0, \quad z = 0 \quad (\text{C.14})$$

Conditions C.12 and C.13 show that at the start of the run the adsorbent does not contain any adsorbed species. And condition C.14 states that at the bed inlet the concentration of the adsorbable specie is maintained constant.  $C$  and  $\bar{q}$  is related by an equilibrium isotherm, the Freundlich equation expressed as

$$q = bCo^p.$$

The basic equations were solved numerically. The intraparticle and bed equations were solved using the Crank-Nicolson implicit method and the explicit finite difference method as presented below.

Bed :

$$\begin{aligned} -D1(\bar{C}_{m+1,n} \frac{-2\bar{C}_{m,n} + \bar{C}_{m-1,n}}{\Delta Z^2}) + U(\bar{C}_{m+1,n} - \bar{C}_{m-1,n}) + \frac{(\bar{C}_{m,n+1} - \bar{C}_{m,n})}{\Delta t} \\ + Kc.a.(\bar{C}_{m,n+1} - C_{i,m,n}) = 0 \end{aligned} \quad (C.15)$$

Rearrange equation C.15 to give the following equation.

$$\begin{aligned} \bar{C}_{m,n+1} = \bar{C}_{m,n}(1-B1-2B3) - B2(\bar{C}_{m+1,n} - \bar{C}_{m-1,n}) + B1(C_{i,m,n}) \\ + B3(\bar{C}_{m+1,n} + \bar{C}_{m-1,n}) \end{aligned} \quad (C.16)$$

$$B1 = \Delta t Kca / \epsilon_s$$

$$B2 = U \Delta t / 2 \epsilon_s \Delta z$$

$$B3 = D1 \Delta t / \epsilon_s \Delta z^2$$

Particle :

$$\begin{aligned} \frac{(q_{r,n+1} - q_{r,n})}{\Delta t} = D_p \left[ \frac{2(q_{r+1,n} - q_{r-1,n})}{2\Delta r} + \frac{(q_{r+1,n} - 2q_{r,n} + q_{r-1,n})}{\Delta r^2} + \right. \\ \left. \frac{(q_{r+1,n+1} - 2q_{r,n+1} + q_{r-1,n+1})}{\Delta r^2} \right] \end{aligned} \quad (C.17)$$

Then equation C.17 becomes the following

$$q_{r,n+1} = A2.q_{r,n} + A3 [ A4.q_{r+1,n} + A5.q_{r-1,n} + \frac{1}{2} (q_{r-1,n+1} + q_{r+1,n+1}) ] \quad (C.18)$$

$$\begin{aligned} A1 &= \Delta t D_p / \Delta r^2 \\ A2 &= (1 - A1) / (1 + A1) \\ A3 &= A1 / (1 + A1) \\ A4 &= 0.5 + \Delta r / r \\ A5 &= 0.5 - \Delta r / r \end{aligned}$$

Where  $n$  is the time index,  $m$  is the column space index and  $r$  is the space index within the particle. The particle was divided into 5 shells. To start the numerical integration, the boundaries C.12 to C.14 were used to solve C.15 to give  $\bar{C}_{m,n+1}$ . Then assume  $C_i$  at the particle surface and calculate  $q_{r,n+1}$  from the relationship between  $q$  and  $C$  using the adsorption isotherm equation. Integration using equation C.10,  $\bar{q}_{m,n+1}$  is performed. The new value of  $\bar{C}_{m,n+1}$  will be set equal to  $(q_{r,n+1})^{1/\beta}$ , then equation C.15 and C.18 are solved anew. To solve these equations the turbo basic program presented below was used.

```
CLEAR
INPUT "CO = ";CO!
INPUT "DS = ";DS!
INPUT "KC = ";KC
INPUT "U = ";U
INPUT "L = ";L : INPUT "M = ";M: Z = L/M
INPUT "TOTAL TIME = ";TT! : INPUT "dt = ";T
N = TT!/T : INPUT "Dia = ";D: INPUT "R = ";R1
dR = D/(2*R1)
INPUT "DL = ";DL
EB! = .68
PB! = .36
AV! = 68.164
DIM C(M,2) : DIM Q(M,2)
DIM I(R1,M) : DIM J(R1,M)
```

```

CLS
LPRINT " Co(mg/ml) =" USING "####.##" ;CO!
LPRINT " Ds(cm /min) =" USING "#####";DS!
LPRINT " Kc(cm/min) =" USING "#####";KC
LPRINT " Dl(cm/min) =" USING "####";DL
LPRINT " U(cm/min) =" USING "####";U
LPRINT " L(cm) =" USING "####";L
LPRINT " Eb =" USING "####";EB!
LPRINT " Pb(g/cm ) =" USING "####";PB!
O = 0
A1 = (T*DS!)/(dR^2) : A2 = (1-A1)/(1+A1):A3 = A1/(1+A1)
B1 = (T*KC*AV!)/EB! : B2 = (U*T)/(2*EB!*Z) :B3 = (DL*T)/(EB!*Z*Z)
FOR H = 2 TO M
  C(H,1) = 0 :Q(H,1) = 0
NEXT H
Q(1,1) = 0
C(1,1) = CO!
LPRINT "--"
LPRINT "-----"
LPRINT " TIME(min) C(mg/ml) C/Co Q"
LPRINT "-----"
TIME = 0
FOR G = 1 TO M
  C(1,2) = CO! : KK = 0
  FOR H = 1 TO M-1
    IF H>1 THEN 350
    CI = CO! : GOTO 370
    350 C(H,2) = C(H,1)*(1-B1-2*B3)-B2*(C(H+1,1)-C(H-1,1))
      +B1*Q(H-1,2)+B3*(C(H+1,1)+C(H-1,1))
    IF C(H,2)<0 THEN C(H,2) = 0
    IF C(H,2)>CO! THEN C(H,2) = CO!
    CI = Q(H-1,2)
  370 IF G>1 THEN 410
    FOR E = 1 TO R1
      I(E,H) = 0
    NEXT E
  410 J(R1,H) = 4.379*CI^-.7447
  430 V = J(R1,H)*((D/2)^2)*dR
    FOR E = R1-1 TO 2 STEP -1
      S = dR*E
      J(E-1,H) = 0
      A4 = .5+(dR/S) : A5 = .5-(dR/S)
      480 J(E,H) = A2*I(E,H)+A3*(A4*I(E+1,H)+
        A5*I(E-1,H)+.5*(J(E-1,H)+J(E+1,H)))
      V = V+J(E,H)*(S^2)*dR
    NEXT E
    J(1,H) = J(2,H)
    V = V+J(1,H)*dR^3
    SUMQ = (3*V)/(D/2)^3
  123 LNQ = LOG(SUMQ)
  125 A9 = (LNQ-1.477)/.7447
    Q(H,2) = EXP(A9)
    KK = KK+(SUMQ*0.4)
  580 FOR E = 1 TO R1
    I(E,H) = J(E,H)
  NEXT E
  NEXT H
  C(M,2) = 1/3*(4*C(M-1,2)-C(M-2,2))
  Q(M,2) = 1/3*(4*Q(M-1,2)-Q(M-2,2))
  TIME = TIME+T
  O = O+1
  PRINT USING "####.##";TIME
  PRINT USING "#####";C(M,2)
  PRINT USING "#####";KK
  IF O<10 THEN 500
  LPRINT TAB(10) USING "####.##";TIME TAB(25)
  USING "#####";C(M,2)TAB(40) USING "####.##";C(M,2)/CO!
  TAB(55) USING "#####";KK
  O = 0
  500 FOR H = 1 TO M
    C(H,1) = C(H,2) : Q(H,1) = Q(H,2)
  NEXT H
  NEXT G
  LPRINT "-----"
  LPRINT "END OF CALCULATION"
600 END

```

## APPENDIX D

## DETERMINATION OF SURFACE DIFFUSION COEFFICIENT

The concentration as a function of with time of n-hexane in mixture of n-hexane and cyclohexane on activated carbon at 15°C are in batch experiments presented in table D1.

TABLE D1

Concentration (C) , dimensionless concentration (E) , and dimensionless time ( $\theta$ ) , as a function of time based on batch experiments.

Time (hr)	Co 170.13 mg/ml			Co 350.86 mg/ml		
	C	E	$\theta$	C	E	$\theta$
1	149.05	0.65	0.03	306.53	0.65	0.03
2	146.45	0.73	0.04	296.30	0.80	0.06
3	144.18	0.80	0.06	296.30	0.80	0.06
4	142.24	0.86	0.08	289.48	0.90	0.11
5	140.94	0.90	0.11	289.48	0.90	0.11
6	140.94	0.90	0.11	289.48	0.90	0.11
7	139.32	0.95	0.15	286.07	0.95	0.15
8	138.35	0.98	0.20	286.07	0.95	0.15
9	137.70	1.00	0.28	282.67	1.00	0.28
10	137.70	1.00	0.28	282.67	1.00	0.28



Intraparticle diffusion coefficients called surface diffusion coefficients if the hypothesis of surface diffusion is made, can be estimated from the correlation presented in figure D.1 (3) when the exponential  $\beta$  and the constant in the Freundlich equation are known. Reading  $\theta$  from figure E.1 for the experimental E values (  $E = \frac{C_0 - C_u}{C_0 - C_{\infty}}$  ) and plotting  $\theta$  against time as shown in figure D.2 gives a straight line through the origin.  $D_s$  is now determined from the value of the slope using the following relation.

$$D_s = \text{slope} \times R^2 \quad (\text{D.1})$$

The average value of  $D_s$  for this study was found to be  $1.0640 \times 10^{-5} \text{ cm}^2/\text{min}$

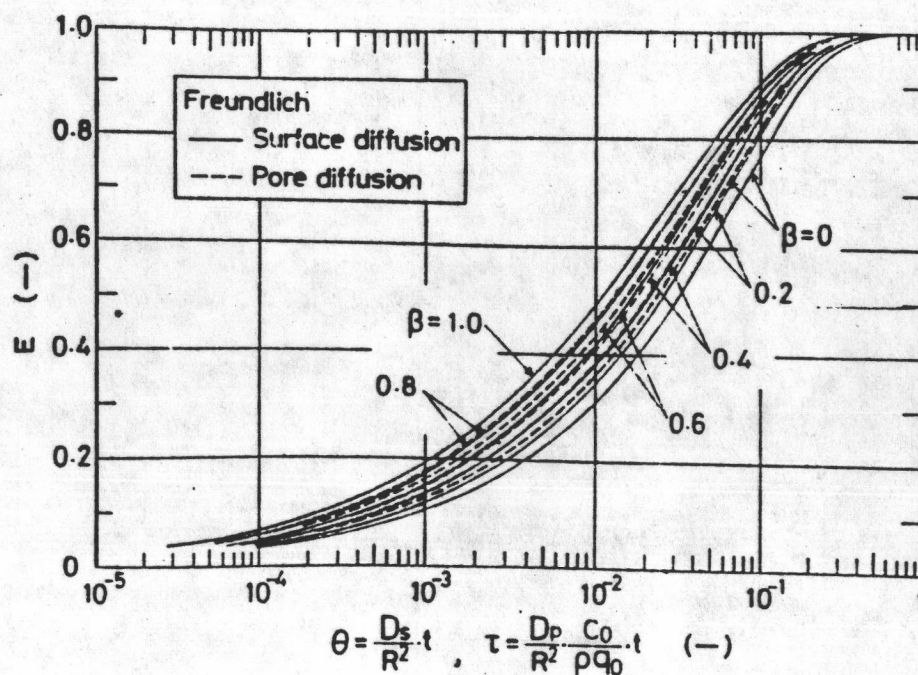


Figure D.1 E vs. dimensionless time for Freundlich isotherms ( $\beta$  = exponent of Freundlich isotherm equation).

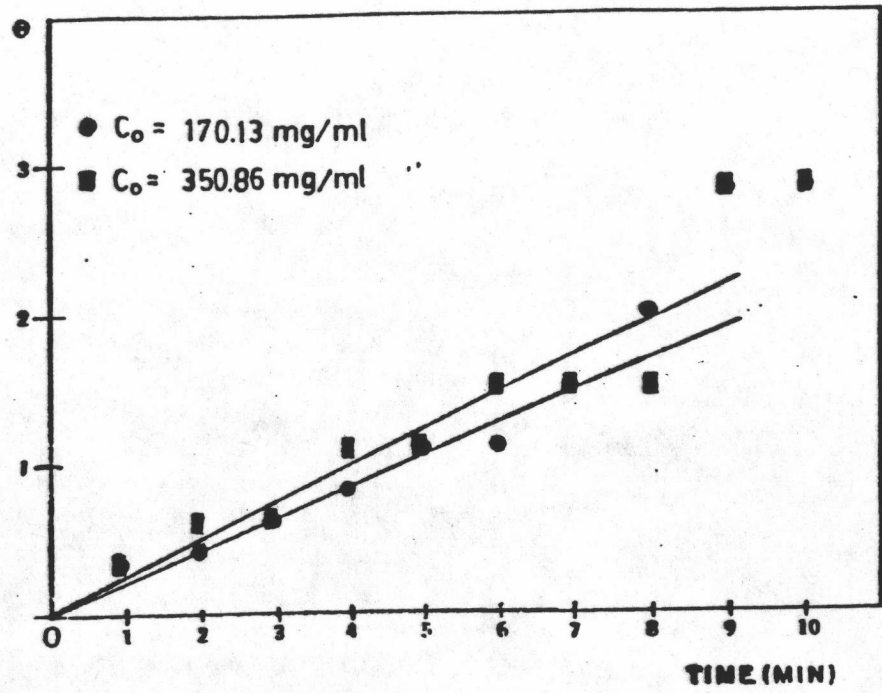


Figure D.2  $\theta$  as a function of time obtained for experimental E values.

## APPENDIX E

## SAMPLE CALCULATION OF THE BREAKTHROUGH CURVE

Surface excess and equilibrium isotherm

Equilibrium concentrations of n-hexane at equilibrium are presented in table B1. A surface excess,  $n_1^s$ , can be calculated from the following equation.

$$n_1^s = \frac{n^t (x_0 - x)}{g} \quad (\text{E.1})$$

where  $n_1^s$  = surface excess, mmole adsorbed/g adsorbent  
 $n^t$  = total mole in solution, mmole  
 $x_0$  = initial mole fraction of A  
 $x$  = equilibrium mole fraction of A  
 $g$  = adsorbent weight, g.

A equilibrium isotherm can be calculated when the adsorption volume is known. The adsorption volume used in this study is 0.852 cm<sup>3</sup>/g. The equilibrium isotherm for liquid phase adsorption will follow the Freundlich equation as follows

$$q = bC^p \quad (\text{E.2})$$

Taking the logarithm of both sides in equation E.2 gives

$$\ln q = \ln b + \beta \ln C \quad (\text{E.3})$$

Plotting  $\ln q$  vs.  $\ln C_0$  may give a straight line, and  $\beta$  and  $b$  are determined from the slope and the intercept. The equilibrium isotherm of n-hexane on activated carbon at 15 C as shown in figure 4.2 is described by the following equation.

$$q = 4.379 C^{0.7447} \quad (\text{E.4})$$

#### Axial dispersion coefficients

The axial dispersion coefficients in packed bed can be calculated from equation E.4. (E.Y. Wen and L.T. Fan, "Model for flow system and chemical reactions")

$$N_{Re} = 0.20 + 0.011 N_{Re}^{0.48} \quad (\text{E.5})$$

equation E.4 can be rearranged to give

$$D_L = \frac{N_{Re}}{0.02 + 0.011 N_{Re}^{0.48}} \quad (\text{E.6})$$

Axial dispersion coefficients obtained from published correlations for different column using equation E.6 are presented in table VIII.

#### External mass transfer coefficients

External mass transfer coefficient can be estimated from

correlation for packed beds (4) as follows.

$$N_{sh} = 1.17 N_{Re}^{0.555} N_{Sc}^{1/3} \quad (E.7)$$

Then rearranged to give

$$k_f = 1.17 \frac{D_v}{D_p} (N_{Re}^{0.555} N_{Sc}^{1/3}) \quad (E.8)$$

The diffusivities of liquid solute in the liquid phase which is generally smaller than in the gas phase by 4 to 5 orders were calculated by the following known equation

$$D_v = 7.4 \times 10^{-8} \frac{(\Psi_B M)^{1/2} T}{\mu V_A^{0.6}} \quad (E.9)$$

$D_v$  = liquid diffusivity,  $\text{cm}^2/\text{sec}$

$T$  = absolute temperature, K

$\mu$  = viscosity, cP

$V_A$  = molar volume of solute as liquid at its normal boiling point,  $\text{cm}^3/\text{g mole}$

$\Psi_B$  = association parameter for solvent, 1 for cyclohexane

$M_B$  = molecular weight of solvent

Data from calculations using equation E.9 is presented in table E1. Molar volume of n-hexane is  $185.40 \text{ cm}^3/\text{g.mole}$ .

#### Overall mass transfer coefficients

The overall mass transfer coefficient,  $K_c$  depend on the

external mass transfer coefficient,  $k_f$ , and an effective internal mass transfer coefficient,  $k_{int}$ . Diffusion within the particle is actually an unsteady-state process. An approximate average coefficient for a sphere can be estimated using following equation.

$$k_{int} = \frac{10D_s}{D_p} \quad (E.10)$$

This leads to

$$\frac{1}{K_c} = \frac{1}{k_f} + \frac{D_p}{10D_s} \quad (E.11)$$

Parameters from the calculations are shown in table VIII.

Table E1

Parameters for prediction of breakthrough curve.

	1	2	3	4	5	6
$C_0$ (mg/ml)	150.27	238.32	332.98	157.35	140.34	139.21
$U_0$ (cm/min)	1.59	1.53	2.90	2.40	2.94	3.70
$\rho_r$ (g/cm <sup>3</sup> )	0.7524	0.7368	0.7201	0.7511	0.7541	0.7543
$\mu$ (cP)	0.8280	0.7400	0.6440	0.8210	0.8380	0.8400
Re	0.2648	0.2793	0.5945	0.6104	0.6104	0.3951
$D_v$ (cm <sup>2</sup> /sec), $\times 10^5$	1.0290	1.1520	1.3230	1.0380	1.0170	1.0960
$N_{sc}$ , $\times 10^{-3}$	1.0691	0.8719	0.6757	1.0528	1.0925	1.0974
$k_f$ (cm/min), $\times 10^3$	3.0871	3.3289	5.4661	4.4557	5.0072	3.8788
$K_c$ (cm/min), $\times 10^5$	9.6425	9.6447	9.6556	9.6517	9.6540	9.6486
$D_l$ (cm <sup>2</sup> /min)	0.6770	0.6482	1.1165	1.1618	1.4191	0.9761

### The breakthrough curves

Breakthrough curves can be solved using a turbobasic program on a personal computer as shown in appendix C . The calculation time is about 1 min for each point on the breakthrough curves. This program was run on an IBM-PC-XT with a 8087 math coprocessor chip. The result of the predicted breakthrough curves at  $C_0 = 150.27$  mg/ml,  $U_0 = 1.59$  cm/min and  $Z = 46$  cm are shown as follows in table E2.  $Q$  is the amount adsorbed in the column calculated from equation C.10.

Table E2

$C_0(\text{mg/ml}) = 150.27$   
 $D_s(\text{cm/min}) = 0.0000010640$   
 $K_c(\text{cm/min}) = 0.0000850000$   
 $D_l(\text{cm/min}) = 0.678$   
 $U(\text{cm/min}) = 1.59$   
 $L(\text{cm}) = 46.00$   
 $E_b = 0.680$   
 $P_b(\text{g/cm}) = 0.360$

TIME(min)	C(mg/ml)	C/Co	Q
0.50	0.0000	0.0000	110.3544
1.00	0.0000	0.0000	111.3133
1.50	0.0000	0.0000	112.2720
2.00	0.0000	0.0000	113.2304
2.50	0.0000	0.0000	114.1887
3.00	0.0000	0.0000	115.1467
3.50	0.0000	0.0000	116.1046
4.00	0.0000	0.0000	117.0622
4.50	0.0000	0.0000	118.0197
5.00	0.0000	0.0000	118.9770
5.50	0.0000	0.0000	119.9342
6.00	0.0000	0.0000	120.8912
6.50	0.0000	0.0000	121.8479
7.00	0.0000	0.0000	122.8046
7.50	0.0000	0.0000	123.7611
8.00	0.0000	0.0000	124.7175
8.50	0.0000	0.0000	125.6737
9.00	0.0000	0.0000	126.6299
9.50	0.0001	0.0000	127.5858
10.00	0.0004	0.0000	128.5417
10.50	0.0019	0.0000	129.4974
11.00	0.0071	0.0000	130.4530
11.50	0.0232	0.0002	131.4087
12.00	0.0674	0.0004	132.3640
12.50	0.1753	0.0012	133.3194
13.00	0.4134	0.0028	134.2747
13.50	0.8911	0.0059	135.2299
14.00	1.7700	0.0118	136.1850
14.50	3.2625	0.0217	137.1401
15.00	5.6157	0.0374	138.0950
15.50	9.0791	0.0604	139.0500
16.00	13.8591	0.0922	140.0048
16.50	20.0720	0.1336	140.9596
17.00	27.7056	0.1844	141.9144
17.50	36.6016	0.2436	142.8691
18.00	46.4653	0.3092	143.8238



18.50	56.8986	0.3785	144.7784
19.00	67.4576	0.4489	145.7331
19.50	77.6998	0.5171	146.6876
20.00	87.2459	0.5806	147.6422
20.50	95.8109	0.6376	148.5967
21.00	103.2219	0.6869	149.5512
21.50	109.4163	0.7281	150.5057
22.00	114.4252	0.7615	151.4603
22.50	118.3495	0.7876	152.4148
23.00	121.3322	0.8074	153.3692
23.50	123.5344	0.8221	154.3238
24.00	125.1156	0.8326	155.2782
24.50	126.2212	0.8400	156.2327
25.00	126.9748	0.8450	157.1872
25.50	127.4762	0.8483	158.1417
26.00	127.8025	0.8505	159.0964
26.50	128.0104	0.8519	160.0509
27.00	128.1406	0.8527	161.0055
27.50	128.2211	0.8533	161.9602
28.00	128.2704	0.8536	162.9148
28.50	128.3009	0.8538	163.8695
29.00	128.3200	0.8539	164.8242
29.50	128.3326	0.8540	165.7791
30.00	128.3415	0.8541	166.7338

-----  
END OF CALCULATION

## APPENDIX F

## DETERMINATION OF PARTICLE SIZES

The particle size distribution of 25x40 mesh particles was determined through microscopy with a spectromicrometer using Ferret's method as shown in figure F1. The size distribution of the particles were found to have the same shape as shown in figure F2. The average diameter used is the surface mean diameter which has the following relationship.

$$\text{surface mean diameter} = d_{sav} = \left( \frac{\sum n d_p^2}{n} \right)^{1/2} \quad (F.1)$$

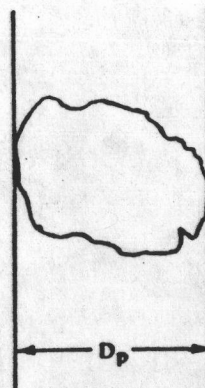


Figure F1 Ferret's diameter, the longest dimension along the line parallel to the base of the view.

The surface mean diameter obtained was 0.11 cm.

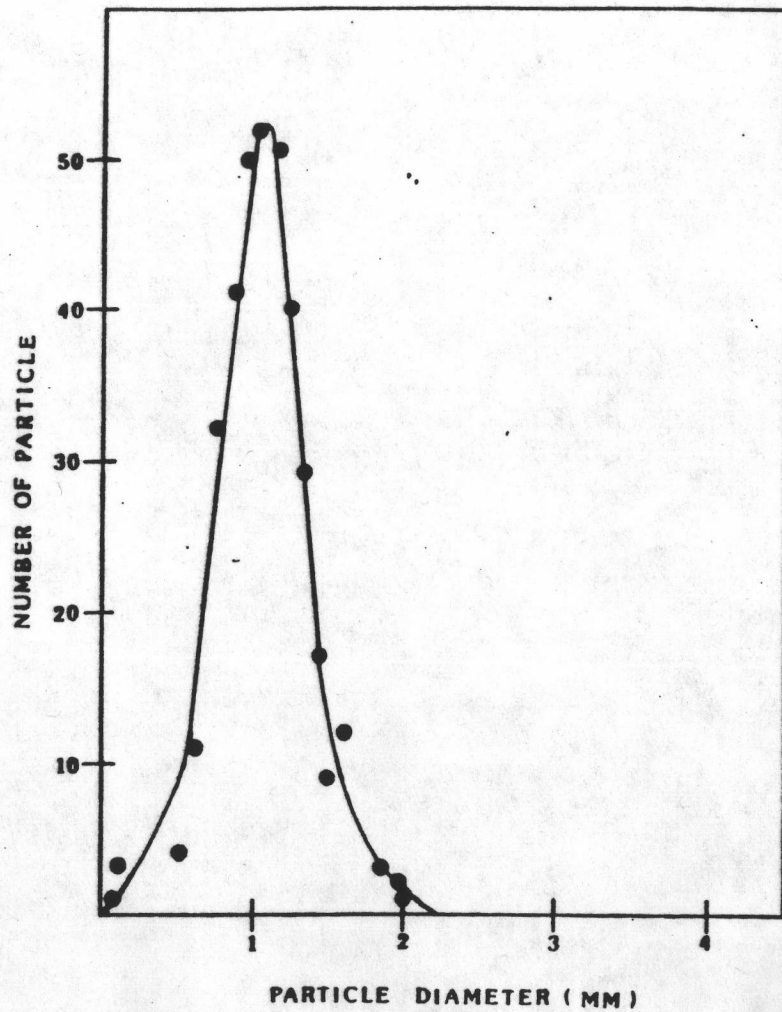
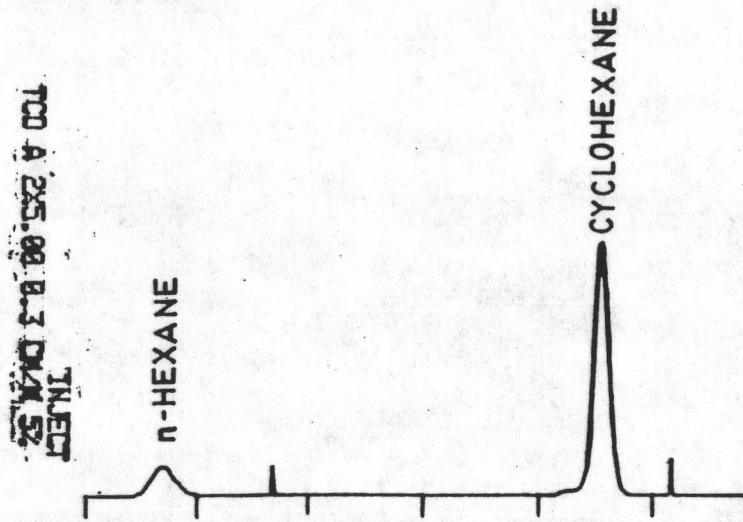


Figure F2 Size distribution of particles with an average size of 0.11 cm.

## APPENDIX G

## EXAMPLE OF CHROMATOGRAPHIC PEAKS



FigureG1 The chromatographic peaks of a binary mixture containing n-hexane and cyclohexane.

## APPENDIX H

## SELECTION ADSORPTION OF HYDROCARBONS IN BINARY MIXTURES

Data obtained by A.E.Hirschler and S.Amon(2) is shown in tables H1 to H3.

Table H1

SELECTIVE ADSORPTION IN PARAFFIN-NAPHTHENE SYSTEMS						
Component A	Component B	Adsorbent	Equilibrium Conc., % of A	Component Adsorbed	Ml. Adsorbed per 100 Grams of Adsorbent	Composition of Point of Zero Selectivity Vol. % (Approx.)
2,2-Dimethylbutane	Cyclopentane	B	..	..	....	87-100% B*
2,2-Dimethylbutane	Cyclopentane	C	10.7	A	0.27	85-100% B*
n-Hexane	Methylcyclopentane	B	80.9 90.7	B B	0.08 0.31	85-90% B
n-Hexane	Methylcyclopentane	C	10.9 89.7	A A	2.1 0.50	U-type, A ads.
n-Hexane	Cyclohexane	B	11.2 80.7 90.0	A A B	>1.0 1.1 0.37	70% A
n-Heptane	Cyclohexane	C	7.4 90.0	A A	>2.0 0.06	U-type, A ads.
2,2-Dimethylbutane	Cyclohexane	B	10.0 47.7 90.0	A B B	0.37 0.12 1.0	65% B
2,2-Dimethylbutane	Cyclohexane	C	0.8 10.0 90.0	A B B	0.10 1.9 1.0	92% B
n-Heptane	Methylcyclohexane	B	10.0 48.7 80.0 90.0	A A A B B	1.2 0.37 0.79 0.11 0.52	87% A
n-Heptane	Methylcyclohexane	C	10.0 90.0 97.0	A A A	4.2 0.78 0.22	U-type, A ads.
2,2,4-Trimethylpentane	Methylcyclohexane	B	10.0 49.8 90.0	A B B	0.12 0.52 0.36	75% B
2,2,4-Trimethylpentane	Methylcyclohexane	C	10.0 90.0	B B	0.42 2.2	U-type, B ads.
2,2,4-Trimethylpentane	Methylcyclohexane	A	9.9 90.0	B B	0.01 0.16	95-100% B
2,4-Dimethylpentane	Cyclohexane	B	10.0 80.0 90.0	A A B	1.1 0.79 0.29	70% A
2,2,6-Trimethylbutane	Cyclohexane	B	10.0 80.0 90.0	A B B	0.41 0.33 0.78	70% B
2,2,6-Trimethylbutane	Cyclohexane	C	10.0 48.0 89.8	A B B	0.61 0.20 2.0	63% B
n-Octane	Ethylcyclohexane	B	10.0 80.0 90.0	A B B	0.20 0.28 0.55	70% B
n-Octane	Ethylcyclohexane	C	10.0 90.7 95.0	A A A	>2.0 0.06 0.01	98-100% A
n-Octane	Ethylcyclohexane	A	9.0 90.7	A A	0.12 0.09	U-Type, A ads.
2,2,4-Trimethylpentane	Ethylcyclohexane	B	9.0 10.0 80.0 90.0	.. B B B	0 0.1 0.67 0.55	90-100% B
n-Decane	Amylcyclohexane	B	10.0 80.0 87.7	A B B	0.22 0.45 0.45	70% B

n-Decane	Amlycyclohexane	C	90.3	A	0.80	U-type, A ads.
n-Dodecane	Amlycyclohexane	C	89.7	A	0.80	U-type, A ads.
n-Dodecane	Dicyclohexyl	C	10.0 90.0	A A	4.3 0.62	U-type, A ads.
n-Pentadecane	Dicyclohexyl	B	10.0 90.0	A B	1.4 0.88	90% A
2,2-Dimethylbutane	Ethylcyclohexane	B	10.0 47.1	A B	0.34 0.77	75% B
n-Octane	Cyclohexane	B	85.8 90.8	A B	0.28 0.84	84% A
n-Decane	Cyclohexane	B	80	B	0.29	
n-Dodecane	Dicyclohexyl	B	10 88 90.8	A A B	1.06 0.11 0.80	80% A

\* Estimated from percolation of impure cyclopentane containing several per cent 2,2-dimethylbutane.

Table H2

TABLE I. SELECTIVE ADSORPTION IN PARAFFIN-PARAFFIN SYSTEMS

Component A	Component B	Adsorbent	Equilibrium Concn., % of A	Component Adsorbed	Ml. Adsorbed per 100 Grams of Adsorbent	Composition of Point of Zero Selectivity, Vol. % (Approx.)
n-Heptane	2,4-Dimethylpentane	B	8.0 94.8	A B	0.41 0.25	.....
n-Heptane	2,3-Dimethylpentane	B	94.8	B	0.30	.....
n-Heptane	2,2,4-Trimethylpentane	C	10.0 90.0	A A	>9.8 2.0	U-type, A ads.
2,4-Dimethylpentane	2,2,2-Trimethylbutane	B	10.0 90.0	A A	1.3 0.12	95-100% A
2,4-Dimethylpentane	2,2,3-Trimethylbutane	C	7.0 90.0	A A	1.7 0.70	95-100% A
2,4-Dimethylpentane	2,3-Dimethylpentane	B	10.0 90.0	A	0.48 0	90% A
2,4-Dimethylpentane	2,3-Dimethylpentane	C	19.0 91.0	B B	1.8 0.21	95-100% B
2,2,4-Trimethylpentane	2,2,2-Trimethylpentane	B	10.0 90.0	A A	1.9 0.18	95-100% A
n-Octane	2,2,4-Trimethylpentane	B	10.0 51.7 90.0	A A B	1.4 0.29 0.86	70% A
n-Octane	2,2,4-Trimethylpentane	C	10.0 86.0 91.9	A A A	9.2 2.7 2.2	U-type, A ads.
n-Octane	2,2,4-Trimethylpentane	A	0.6 80.8	A B	0.06 0.08	~80% A
n-Heptane	n-Pentadecane	B	10.0 90.0	A A	0.97 1.1	U-type, A ads.
n-Heptane	n-Hexadecane	C	10.0 90.0	B B	0.68 >7.8	U-type, B ads.
n-Heptane	n-Heptadecane	A	10.0 90.0	B	0 0.14	90% B
n-Octane	n-Decane	B	11.7 90.8	A A	0.46 0.17	U-type, A ads.
n-Octane	n-Decane	C	10.0 90.0	B B	0.51 1.8	U-type, B ads.
n-Hexane	2,2,2-Trimethylbutane	C	9.2 80.4 91.1	A A A	74.2 8.4 2.1	U-type, A ads.

\* B silica gel, C carbon, A alumina.

Table H3

TABLE III. SELECTIVE ADSORPTION IN NAPHTHENE-NAPHTHENE SYSTEMS

Component A	Component B	Absorbent	Equilibrium Concn., % of A	Component Adsorbed	Ml. Adsorbed per 100 Grams of Adsorbent	Composition of Point of Zero Selectivity, Vol. % (Approx.)
Cyclopentane*	Cyclohexane	B	10.0 90.0	A	>0.83 0.84	U-type, A ads
Cyclopentane*	Cyclohexane	C	10.0 90.0	A	1.1 Little change	90-100%
Methylcyclopentane	Cyclohexane	B	10.0 90.0	A	0.88 0.87	U-type, A ads
Methylcyclopentane	Cyclohexane	C	10.0 90.0	A	2.1 0.90	U-type, A ads
Cyclohexane	Ethylcyclohexane	B	10.0 88.0 90.0	A B	0 0.78 0.10	70% B
Cyclohexane	Ethylcyclohexane	C	14.8 88.0	B B	1.7 >2.4	U-type, B ads
Methylcyclohexane	Ethylcyclohexane	B	80.0	A	0.18	.....
Methylcyclohexane	Ethylcyclohexane	C	10.0 90.0	B B	1.9 2.2	97-100% B
Methylcyclohexane	Ethylcyclohexane	A	10.0 91.2	A B	0.01 0.18	85% B
Methylcyclohexane	Amylcyclohexane	B	8.9 48.0 90.1	A A B	0.29 0.22 0.28	88% A
cis-Decalin	trans-Decalin	B	..	..	....	98-100% B
Amylcyclohexane	Dicyclohexyl	B	10.0 90.0	A A	>0.48 0.68	98-100%
2-Butylcyclopentylcyclopentane	Dicyclohexyl	B	10.0 90.0	A A	0.61 0.10	98-100% A
Cyclohexane	Dicyclohexyl	C	10.0 90.0	B B	0.78 >4.5	U-type, B ads
trans-Decalin	Dicyclohexyl	C	11.0	A	0.87	

\* Contained several per cent of 2,2-dimethylbutane.

## APPENDIX I

## DETERMINATION OF PORE VOLUME AND VOID FRACTION OF ACTIVATED CARBON

The knowledge of pore volume and bed void fraction for the adsorbent bed used is necessary for the design of adsorbent columns ( i.e. for the calculation of the breakthrough curves). In the absence of proper equipment the following method was used.

The method involved placing a know weight of adsorbent (about a gram) in a graduated glass cylinder ( 10 ml) the adding 2 ml of an adsorbable liquid , in this case n-hexane. After mixing the entire mixture so that adsorption takes place fully total volume recorded is now the volume of the n-hexane plus volume of the solid which is impermeable to water. It was assumed that no hexane has evaporated and that there was complete filling of the pores. It is to be noted that the system is composed of 3 volumes : the liquid outside the pellets , the liquid inside the pellet , and the solid inside the pellet. This first value measured is the solid inside the pellets ,  $V_s$ .

We now drain the liquid out of the system which means that the adsorbent pellets remain with pores filled with liquid. We then add 2 ml of n-hexane in the cylinder once again. The total volume of n-hexane is now the volume of the n-hexane added last (2 ml) plus the volume of the liquid inside the pores. Thus we know by difference the volume of the solid plus the pore volume,  $V_s + V_p$ .

Then in this second addition of n-hexane we can measure the bulk volume of the bed  $V_b$ . The porosity is equal to



$(V_b - V_p + V_p) / V_b$ . The experimental data is presented in table 11.

Table 11

Experimental data for pore volume ( $V_p$ ) and void fraction ( $\epsilon$ ).

	Pore volume $V_p$ (ml/g)	Void fraction
1	0.897	0.685
2	0.788	0.680
3	0.907	0.695
4	0.902	0.580
5	0.871	0.740
6	0.700	0.748
average	0.680	0.852



## AUTOBIOGRAPHY

Wilawan Keawniyomchaisri was born on February 7, 1963 in Nakorn Pathom Province, Thailand. She attended Benjamarachalai High School in Bangkok and graduated in 1980. She received her Bachelor of Science Degree in Chemistry from Silapakorn University, Thailand in April 1984. Following her graduation, she worked with the Technical Equipment Co.,Ltd. for two years. She enrolled for a Master's Degree program in chemical engineering at Chulalongkorn University in 1986. She was granted a Master of Engineering degree in May 1990.