

ADSORPTION EQUILIBRIA OF BENZENE ON ACTIVATED CARBON IN THE PRESENCE OF SUPERCRITICAL CARBON DIOXIDE

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The adsorption equilibrium loadings of benzene on Toyo Calgon's BPL activated carbon in the presence of supercritical carbon dioxide were measured by time integration of the breakthrough curves at temperatures of 313.2 and 333.2 K and pressures from 0.99 to 11.87 MPa. The benzene loadings were observed to decrease with increasing pressure, even at low pressures far below the critical point, implying the effect of carbon dioxide adsorption over the amount of adsorbed benzene and solvent power of carbon dioxide. The equilibrium data were correlated by the Dubinin-Astakhov equation. Inclusion of pressure dependence in two parameters was found to be necessary in order to apply the pure component Dubinin-Astakhov equation to the studied system.

Introduction

Supercritical fluids are expected to replace conventional solvents for extraction processes in a growing number of applications, because of their liquid-like solvent power and gas-like mass transfer properties, as well as the possibility of imposing large changes on those properties by minor adjustments of pressure and temperature. Effective application of supercritical fluids in extraction processes, however, requires an efficient process to remove the extract from the supercritical fluid, in order to recycle it. The generally suggested separation method is solubility reduction by pressure control, but this requires a large amount of energy to recompress the supercritical fluid after the separation process. In contrast to this, recompression is minimal in the case of an adsorption separation method, in which the impurity is removed from the supercritical fluid by adsorption on an adsorbent at constant pressure. Adsorption separation stands out, in this context, as a potentially advantageous process from the energetical point of view.

Adsorption under supercritical fluids has been studied by a number of researchers, notably in applications of supercritical chromatography²⁾ or regeneration of adsorbent by desorption with supercritical fluid^{8, 12)}. However, comprehensive adsorption equilibrium data under supercritical conditions are still scarce. Deserving mention the works of Kander and Paulaitis⁴⁾, for phenol on activated carbon, and of Tan and Liou¹³⁾, for toluene.

In the first part of this study, measurements of the adsorption equilibrium of benzene from supercritical carbon dioxide on activated carbon are presented, while the second part¹¹⁾ concerned with adsorption dynamics.

Both equilibrium data and dynamic parameters are necessary for the design of an adsorption process. Carbon dioxide has been the solvent almost universally considered for applications of supercritical fluid technology, and was thereof chosen as the supercritical fluid. Benzene, as a polymer impurity extractable by supercritical carbon dioxide, was selected as the adsorbate, while the adsorbent was activated carbon.

1. Experimental Apparatus and Procedure

Figure 1 shows an outline of the employed experimental apparatus. It basically employs a fixed bed adsorption process, divided into four general sections: gas compression, adsorption, concentration measurement and flow rate measurement.

In the gas compression section, the sample gas, a mixture of benzene (99.5% purity, provided by Katayama Kagaku Co.) and carbon dioxide (99.0% purity, provided by Mitsubishi Kasei Co.), is stored in a cylinder (3.5 l). The gas exits the cylinder and is dried by a zeolite (Tosoh A-3, 8-10 mesh) column, and compressed by a pump (JASCO 880-PU) to the desired experimental pressure. The pressure is monitored by a Bourdon tube pressure gage (Nagano, full-scale 250 kg/cm², $\pm 0.2\%$ F.S.).

The adsorption column is prepared in the following manner. First, the pellets of activated carbon are grinded, sieved to 0.09–0.15 mm diameter, washed in hot water and dried under vacuum. Then, the activated carbon is packed, under vibration, in a 70-mm-long, 7.5-mm-i.d. SUS 316 steel tube. Before use, the activated carbon is regenerated by flowing pure carbon dioxide for 2 hours at 333 K and 20 MPa. During the experiments, the column is immersed in a constant temperature water bath (Yamato BK-43, maxi-

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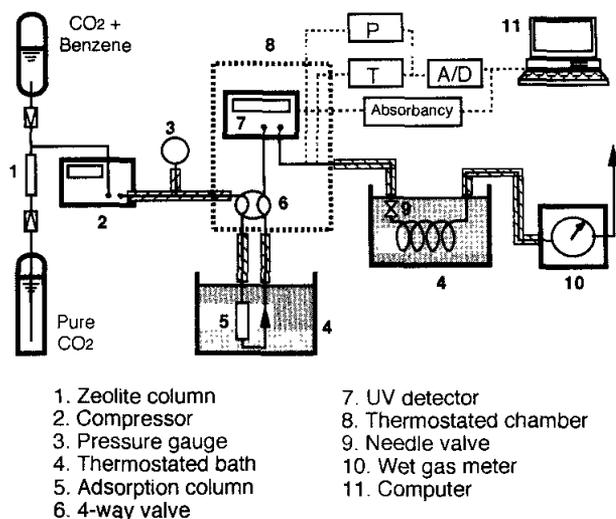


Fig. 1 Schematic diagram of experimental apparatus

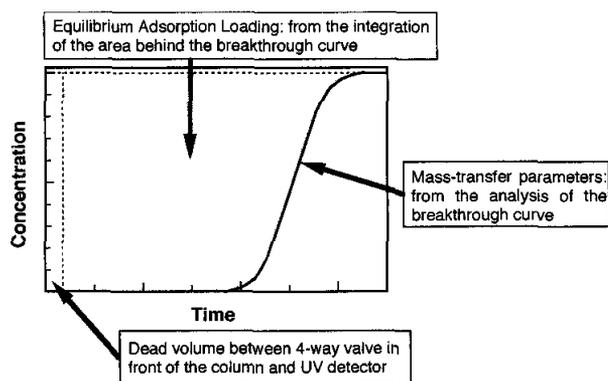


Fig. 2 Breakthrough curve

imum deviation ± 0.05 K).

The concentration at the outlet of the column is monitored by a UV detector (JASCO 875-UV) placed inside a thermostated chamber. The measured absorbance is automatically collected by a computer (NEC PC-9801), together with the values of temperature and pressure measured by the detectors (an Okano T-35-200-BK-9-C-200-EXC thermocouple, max. dev. ± 0.05 K and a Druck PDCR330 semiconductor pressure sensor, max. dev. $\pm 0.15\%$ F.S.).

After the concentration measurement, the gas is decompressed by a needle valve and sent to a wet gas flow meter (Shinagawa W-NK-1B), and then discharged to the atmosphere.

In the adsorption experiment, pure carbon dioxide flows through the system (including the adsorption column), first at the experimental temperature, pressure and flow rate, and under these conditions the UV detector is set to zero. Then, the 4-way valve (Rheodyne) is switched, isolating the column from the rest of the system, and the sample gas flows through the system. At time zero, the 4-way valve is switched again, allowing the sample gas to enter the adsorption column, while the concentration of benzene at the outlet of the column is continuously measured by the UV detector. The experiment ends when

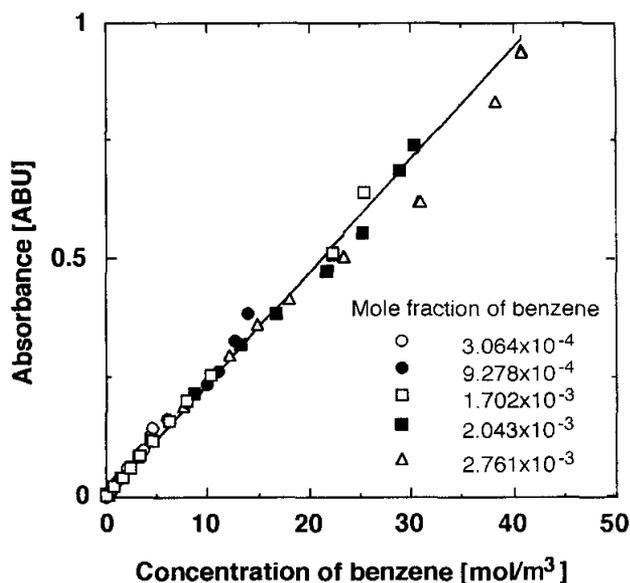


Fig. 3 Calibration curve of UV detector

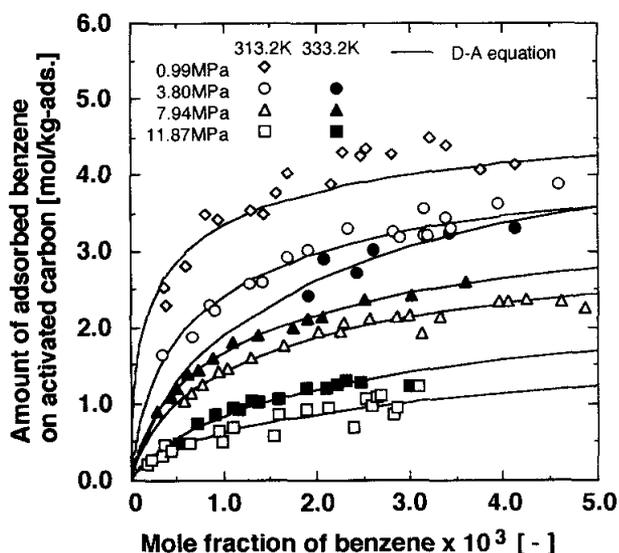


Fig. 4 Adsorption equilibrium isotherms

the outlet concentration equals the inlet concentration, meaning that equilibrium has been achieved. The plot of outlet benzene concentration vs. time recorded in the computer (breakthrough curve) yields the equilibrium data and information on the adsorption dynamics, as shown in Fig. 2.

The adsorption loading is obtained by time integration of the breakthrough curve. Conversion of the absorbance read by the UV detector to benzene concentration is necessary for the calculation of the equilibrium adsorption loading. To this end, use was made of a calibration curve, obtained by measurement of the absorbance of mixtures of benzene and carbon dioxide at known concentrations and supercritical conditions (313.2 K and up to 10.5 MPa), according to the following procedure. First, known amounts of benzene and carbon dioxide were introduced into a previously evacuated cylinder, which was then gradually decompressed at constant temperature, caus-

Table 1. Experimental data for amount of adsorbed benzene on activated carbon at 313.2 K

$y \times 10^3 [-]$		$q [\text{mol/kg-ads.}]$
0.99MPa		
0.371		2.522
0.373		2.301
0.591		2.805
0.814		3.486
0.943		3.426
1.299		3.527
1.445		3.483
1.574		3.778
1.691		4.019
2.164		3.881
2.275		4.297
2.475		4.252
2.520		4.362
2.798		4.276
3.206		4.505
3.388		4.408
3.753		4.080
4.138		4.154
3.80MPa		
0.336		1.637
0.680		1.878
0.853		2.305
0.905		2.237
1.274		2.581
1.411		2.607
1.685		2.935
1.911		3.013
2.332		3.304
2.829		3.252
2.904		3.197
3.146		3.549
3.148		3.215
3.195		3.260
3.381		3.451
3.963		3.634
4.590		3.895
7.94MPa		
0.569		1.045
0.653		1.138
0.765		1.251
0.943		1.418
1.050		1.460
1.300		1.591
1.642		1.759
2.029		1.956
2.254		1.944
2.303		2.063
2.573		2.106
2.865		2.137
3.005		2.164
3.136		1.929
3.324		2.135
3.957		2.335
4.048		2.350
4.246		2.378
4.614		2.341
4.874		2.257
11.87MPa		
0.187		0.208
0.231		0.260
0.353		0.326
0.368		0.464
0.443		0.396
0.631		0.484
0.950		0.631
0.981		0.492
1.108		0.678
1.538		0.583
1.592		0.844
1.876		0.911
2.118		0.953
2.392		0.693
2.526		1.051
2.595		0.971
2.642		1.085
2.695		1.112
2.817		0.857
2.853		0.935
3.099		1.226

ing a change in the gas density. Since the benzene mole fraction was very small, the mixture density was approximated to that of pure carbon dioxide, according to the IUPAC table¹⁾. The benzene concentration could then be obtained from the gas density and benzene mole fraction. The absorbance of the mixture was constantly measured, and subtraction of the absorbance of pure carbon dioxide, determined in a separate experiment, yielded the relation between absorption and benzene concentration. **Figure 3** shows the obtained calibration curve, which could be

Table 2. Experimental data for amount of adsorbed benzene on activated carbon at 333.2 K

$y \times 10^3 [-]$		$q [\text{mol/kg-ads.}]$
3.80MPa		
1.900		2.406
2.080		2.906
2.430		2.722
2.600		3.017
3.170		3.192
3.430		3.235
4.140		3.294
7.94MPa		
0.290		0.896
0.430		1.086
0.500		1.198
0.610		1.385
0.740		1.433
0.880		1.594
1.100		1.802
1.380		1.911
1.740		1.997
1.910		2.122
2.060		2.129
2.510		2.381
3.020		2.406
3.610		2.598
11.87MPa		
0.519		0.485
0.716		0.743
0.915		0.841
1.110		0.945
1.170		0.914
1.300		1.032
1.380		1.015
1.590		1.072
1.890		1.191
2.000		1.223
2.120		1.201
2.220		1.251
2.320		1.290
2.470		1.274

approximated to the following linear equation until 1.0 ABU:

$$ABS = 2.37 \times 10^{-2} C \quad (1)$$

where *ABS* is absorbance [ABU], and *C* is concentration of benzene [mol/m³].

2. Results of Adsorption Equilibrium

The measured equilibrium adsorption loadings are shown in **Fig. 4**, while **Tables 1 and 2** list the measured values. We can see from the figure that, contrary to the generally observed behavior in gas adsorption near atmospheric pressure, the equilibrium adsorption loading decreases with increases in pressure. This may be surprising if we neglect the adsorption and solvent power of carbon dioxide, and regard it as an inert carrier fluid. However, the effect of carbon dioxide adsorption and solvent power must be taken into account, as observed by other researchers¹⁴⁾. We can say that the amount of adsorbed benzene will be ultimately determined by the competition between two different interactions: benzene - carbon dioxide - activated carbon in the adsorbed phase and benzene - carbon dioxide in the fluid phase. As pressure increases, a larger amount of carbon dioxide is adsorbed, competing with the adsorption of benzene: at the same time, the solubility of benzene in the carbon dioxide is enhanced. As a result, the benzene adsorption loading decreases with increasing pressure.

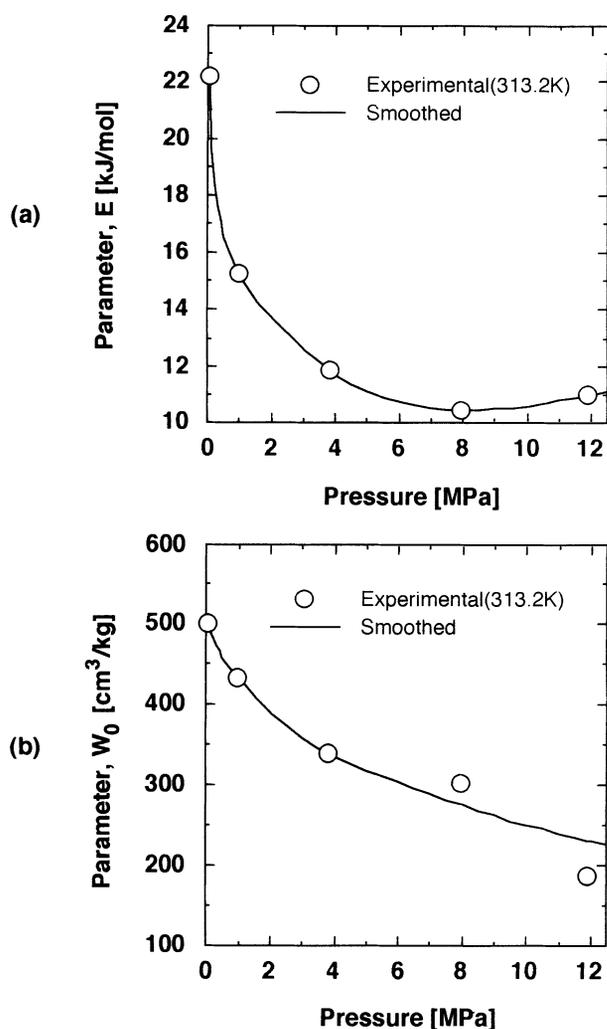


Fig. 5 Pressure dependence of (a) affinity parameter E and (b) limiting adsorption volume W_0 at 313.2 K

3. Correlation by Dubinin-Astakhov Equation

There are a number of adsorption isotherm equations that can be used to correlate experimental data. The simplest is the Langmuir equation, which will be adopted in Part II¹¹⁾ for its convenience in mathematical handling. However, the Dubinin-Astakhov equation has the advantage of permitting thermodynamical estimation of the equilibrium adsorption loading, and for that reason its application to the present system was considered. It can be expressed by equations (2) to (4):

$$W / W_0 = \exp[-(A/E)^n] \quad (2)$$

$$W = q / \rho_s \quad (3)$$

$$A = RT \ln(f_s / f) \quad (4)$$

where n [-] is related to the ratio between adsorbent pore diameter and adsorbate molecular diameter⁵⁾; E [J/mol] is related to the affinity between adsorbent and adsorbate¹⁵⁾; and W_0 [m³/kg-ads.] expresses the limiting adsorption volume, which is the total volume of pores in which adsorption is possible¹⁵⁾. Although we can expect benzene and

Table 3. Values of Dubinin-Astakhov equation

Pressure [MPa]	W_0 [cm ³ /kg-ads.]	E [kJ/mol]
313.2K		
0.024	501	22.18
0.99	434	15.25
3.80	339	11.88
7.94	301	10.45
11.87	186	11.00
333.2K		
3.80	426	9.87
7.94	332	11.28
11.87	253	10.81

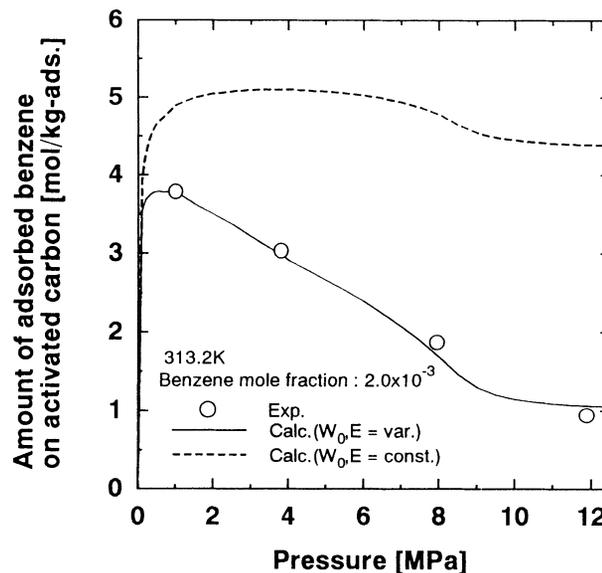


Fig. 6 Benzene adsorption loadings at 313.2 K correlated by Dubinin-Astakhov equation

carbon dioxide to interact at the activated carbon surface, in this study the fugacity and density of benzene in the adsorbed phase were assumed to be the same as those of pure liquid benzene at the system temperature and saturated vapor pressure. The fugacity of benzene in the vapor phase was calculated by modified the BWR equation proposed by Nishiumi *et al.*⁹⁾. Values of the binary parameter k_{12} were determined as 0.069 (313.2 K) and 0.092 (333.2 K) by correlation of vapor-liquid equilibrium data^{3, 7, 10)}.

The parameters n , E and W_0 were determined as follows.

By modification of equation (2):

$$\ln W = -(1/E)^n A^n + \ln W_0 \quad (5)$$

The plot $\ln W$ vs A^n (adsorption characteristic curve) should result in a straight line. The parameter n is selected so that the resulting curve is a straight line, what in the present study was found to be $n = 2$ for all conditions. The parameters E and W_0 are obtained from the curve slope and axis intercept, respectively.

In the present study, the activated carbon is saturated with carbon dioxide before admission of the sample gas. Since the carbon dioxide adsorption loading varies with pressure, we can expect the affinity between adsorbent and adsorbate and the benzene limit adsorption volume (parameters E and W_0) to be affected by changes in pressure.

Values for E and W_0 were determined for each pressure, and their variation with pressure at 313.2 K is shown in **Fig. 5 (a)** and **(b)**. Both decrease with increases in pressure, a behavior that can be related to increases of the carbon dioxide adsorption loading. In the case of the parameter E , the adsorption of carbon dioxide competes with the adsorption of benzene, reducing the interaction between benzene and the adsorbent. In the case of W_0 , the adsorption of carbon dioxide would reduce the adsorbent volume available for adsorption of benzene.

In order to obtain the values at low pressure in the figure, adsorption loadings of pure benzene were measured in a separate experiment by a gravimetric method such as that of Kawazoe *et al*⁽⁶⁾. In the adsorption experiment, activated carbon in a glass cell was heated and exhausted. Benzene vapor introduced was then into the cell. When the pressure variation as read by a Baratron pressure gauge decreased, the glass cell was removed. The adsorption loadings were determined by the weight variation of the cell before and after the adsorption.

The solid lines in Fig. 4 show the results of the adsorption loading calculation according to the above-described procedure, while **Table 3** lists the values of the parameters found for each condition. The solid line in **Fig. 6** shows the variation of adsorption loading with pressure for a 0.0020 benzene mole fraction in the gas phase. For the sake of comparison, the broken line shows the results assuming constant E and W_0 , obtained for pure benzene. As observed in the figure, the assumption of pressure-independent parameters does not fit well for all the experimental data.

Conclusion

The equilibrium loadings of benzene in supercritical carbon dioxide were measured over a broad range of pressures by integration of the breakthrough curve. For all experimental conditions, the benzene loading decreased with increasing pressure. An explanation for the phenomenon is the enhancement of benzene solubility in supercritical carbon dioxide at higher pressures, as well as the effect of carbon dioxide adsorption on the activated carbon.

The data were correlated by the Dubinin-Astakhov equation, including pressure dependent terms. The estab-

lishment of a thermodynamic model for the binary adsorption equilibrium might help to improve the generality of the Dubinin-Astakhov equation, permitting estimation of the mixture parameters from pure-component data, and eliminating the pressure dependence of parameters.

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Nomenclature

A	= adsorption potential	[J/mol]
ABS	= absorbance	[ABU]
C	= concentration of benzene	[mol/m ³]
E	= parameter of Dubinin-Astakhov equation	[J/mol]
f	= benzene fugacity in gas phase	[Pa]
f_s	= benzene fugacity in adsorbed phase	[Pa]
n	= parameter of Dubinin-Astakhov equation	[-]
q	= benzene adsorption loading	[mol/kg-ads.]
R	= universal gas constant	[J/mol.K]
T	= absolute temperature	[K]
W	= adsorption volume	[m ³ /kg-ads.]
W_0	= parameter of Dubinin-Astakhov equation	[m ³ /kg-ads.]
ρ_s	= benzene density in adsorbed phase	[mol/m ³]

Literature Cited

- 1) Angus, S., B. Armstrong and K.M. deReuck: "International Thermodynamic Tables of the Fluid State-3, Carbon Dioxide," IUPAC Project Centre, Pergamon Press (1976)
- 2) Erkey, C. and A. Akgerman: *AIChE J.*, **36**, 1715-1721 (1990)
- 3) Gupta, M.K., Ying-Hsiao, B.J. Huisey and R.L. Robinson: *J. Chem. Eng. Data*, **27**, 55-57 (1982)
- 4) Kander, R.G. and M.E. Paulaitis: In "Chemical Engineering and Supercritical Conditions," J.M. Penninger, R.D. Gray and P. Davidson, eds., p. 461-476, Ann Arbor Science, Ann Arbor (1983)
- 5) Kawazoe, K., V.A. Astakhov and T. Kawai: *Seisan Kenkyu*, **22**, 491-494 (1970)
- 6) Kawazoe, K., V.A. Astakhov, T. Kawai and Y. Eguchi: *Kagaku Kogaku*, **35**, 1006-1012 (1971)
- 7) Kim, C.H., P. Vimalchand and M.D. Donohue: *Fluid Phase Equilibria*, **31**, 299-311 (1985)
- 8) McHugh, M. and V. Krukoni: "Supercritical Fluid Extraction," p. 118-130, Butterworths, Stoneham (1986)
- 9) Nishiumi, H., S. Saitou: *J. Chem. Eng. Japan*, **8**, 356-360 (1975)
- 10) Ohgaki, K., T. Katayama: *J. Chem. Eng. Data*, **21**, 53-55 (1976)
- 11) Porto, J. S., K. Tanida, Y. Sato, S. Takishima and H. Masuoka: *J. Chem. Eng. Japan*, in press
- 12) Tan, C.S. and D.C. Liou: *Ind. Eng. Chem. Res.*, **27**, 988-991 (1988)
- 13) Tan, C.S. and D.C. Liou: *Ind. Eng. Chem. Res.*, **29**, 1412-1415 (1990)
- 14) Wu, Y.Y., D.S.H. Wong and C.S. Tan: *Ind. Eng. Chem. Res.*, **30**, 2492-2496 (1991)
- 15) Yang, R.T. and S.J. Dong: *Ind. Eng. Chem. Res.*, **27**, 630-635 (1988)