

REFERENCES

- Bai, S., Sridhar, S. and Khan, A.A. (2000). Recovery of propylene from refinery off-gas using metal incorporated ethylcellulose membranes. Journal of Membrane Science, 174, 67-79.
- Baker, R.W., Koros, E.L., Cussler, R.L., Riley, W.E., and Strathamann, H. (1991). Membrane Separation Systems, Recent Developments and Future Directions. Noyes data corporation.
- Battal , T., Bac, N., and Yilmaz, L. (1995). Effect of feed composition on the performance of polymer-zeolite mixed matrix gas separation membranes. Journal of Separation Science and Technology, 30(11), 2365-2384.
- Bungay P.M., Lonsdale H.K., and de Pinho, M.N. (eds.) (1983). Synthetic membranes: science, engineering and applications. NATO ASI series. Series C: Mathematical and Physical Sciences, 181, Dordrecht, Holland.
- Grant, M.H. (1991). Membrane technology. Encyclopedia of Chemical Technology, 16, 135-193.
- Ho, W.S., and Dalrymple, D.C. (1994). Facilitated transport of olefin in Ag^+ containing polymer membranes. Journal of Membrane Science, 91, 13-25.
- Ho, W.S., Doyle, G., Savage, D.W., and Pruett, R.L. (1988). Olefin separation via complexation with cuprous diketonate. Industrial Engineering Chemical Research, 27, 334-337.
- Hsiue, G.H., and Yang, J.S. (1996). Polymeric complex membrane for olefin/paraffin separation. Macromolecule Symposium, 105, 51-58
- Hughes, R.D., Mahoney, J.A., and Steigelman, E.F. (1986). Olefin separation by facilitated transport membranes. Recent Developments in Separation Science: CRC Press, Boca Raton, FL., USA.

- Ito, A., and Hwang, S.T. (1989). Permeation of propane and propylene through cellulosic polymer membranes. Journal of Applied Polymer Science, 38, 483-490.
- LeBlance, O.H., Ward, W.J., Matson, S.L., and Kimura, S.G. (1980). Facilitated transport in ion-exchange membranes. Journal of Membrane Science, 6, 339.
- Lloyd, D.R. (1985). Material science of synthetic membranes. American Chemical Society Series, Washington, D. C.
- MacCabe, W.L., Smith, J.C., and Harriott, P. (1993). Membrane separation process. Unit Operations of Chemical Engineering, 5th ed., Singapore: MaGraw-Hill.
- Kesting, R.E., and Fritzsche, A.K. (1993). Polymeric gas separation membrane. John Wiley & Sons Inc.
- Koros, W. J., and Jones, O. W. (1994). U.S. Patent 5 288 304.
- Kulprathipanja, S., and Kulkarni, S.S. (1986). U.S. Patent 4 608 060.
- Kulprathipanja, S., Neuzil, R.W., and Li, N.N. (1988a). U.S. Patent 4 737 165.
- Kulprathipanja, S., Neuzil, R.W., and Li, N.N. (1988b). U.S. Patent 4 740 219.
- Kulprathipanja, S., Neuzil, R.W., and Li, N.N. (1988c). U.S. Patent 4 751 104.
- Kulprathipanja, S., Neuzil, R.W., and Li, N.N. (1992). U.S. Patent 5 127 925.
- Orthmer, K. (1981). Encyclopedia of Chemical Technology, 13, 352.
- Paul, D.R., and Kemp, D.R. (1973). The diffusion time lag in polymer membranes containing adsorptive fillers. Journal of Polymer Science: Syposium, 41, 79-93.
- Rosback, D.H., and Neuzil, R.W. (1977). US. Patent 3 969 223.

- Rousseau, W. (1987). Handbook of Separation Process Technology. John Wiley & Sons Inc.
- Sawyer, L.C., and Grubb, D.T. (1996). Polymer Microscopy, 2nd ed., London: Chapman & Hall.
- Scott, K., and Hughes, R. (1996). Industrial Membrane Separation Technology. Blackie Academic & Professional.
- Serivalsatit, V. (1999). The mechanism of the mixed matrix membrane separation (polyethylene glycol/silicone rubber) for polar gases. M.S. Thesis in the Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand.
- Singh, A., and Koros, W.J. (1996). The significance of entropic selectivity for advanced gas separation membranes. Industrial Engineering Chemical Research, 35, 1231.
- Sridhar, S., and Khan, A.A. (1999). Simulation studies for the separation of propylene and propane by ethylcellulose membrane. Journal of Membrane Science, 159, 209-219.
- Staudt, B.C., and Koros, J.W. (2000). Olefin/paraffin gas separations with 6FDA-based polyimide membranes. Journal of Membrane Science, 170, 205-214.
- Stern, S. A., Shah, V. M., and Hardy, B. J. (1987). Structure-permeability relationships in silicone polymers. Journal of Polymer Science: Part B: Polymer Physics, 25, 1263-1298.
- Suer, M.G., Bac, N., Yilmaz, L., Gurkan, T., and Sacco A., Jr. (1994). Gas separation with zeolite based polyethersulfone membranes. Gas Separation Technology, 11, 661-669.
- Sukapintha, W. (2000). Mixed matrix membrane for olefin/paraffin separation. M.S. Thesis in the Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand.

- Sungpet, A., Way, J.D. Thoen, P.M., and Dorgan, J.R. (1997). Reactive polymer membranes for ethylene/ethane separation. Journal of Membrane Science, 136, 111-120.
- Tantekin, S.B., Atalay, O.C., Tater, M., Erdem, S.A., Scoeman, B., and Sterete, J. (2000). Effect of zeolite particle size on the performance of polymer-zeolite mixed matrix membranes. Journal of Membrane Science, 175, 285-288.
- Teramoto, M., Matsuyama, H., Yamashiro, T., and Katayama, Y. (1986). Separation of ethylene from ethane by supported liquid membrane containing silver nitrate as a carrier. Journal of Chemical Engineering of Japan, 19(5), 419-424.
- Tsou, D.T., Blachman, M.W., and Davis, J.C. (1994). Silver-facilitated olefin/paraffin separation in liquid membrane contractor system. Industrial Engineering Chemical Research, 33, 3209 -3216.
- Yang, J.S., and Hsiue, G.H. (1997). Selective olefin permeation through Ag (I) contained silicone rubber-graft-poly(acrylic acid) membranes. Journal of Membrane Science, 126, 139-149.
- Yang, J.S., and Hsiue, G.H. (1998). Swollen polymeric complex membranes for olefin/paraffin separation. Journal of Membrane Science, 138, 203-211.
- Zimmerman, C.M., Singh, A., and Koros, W.J. (1997). Tailoring mixed matrix composite membranes for gas separations. Journal of Membrane Science, 137, 145-154.



APPENDIX

Mathematical Derivation of Equilibrium Selectivity of Hexene/n-Hexane on adsorbents in adsorption process

Feed 1 = 1 gram of n-hexane + 1 gram of hexene + 18 grams of i-octane =
20 grams

Sample 1 = 1 gram of NaX-zeolite + feed 5 grams = 6 grams

Sample 2 = 1 gram of Silicalite + feed 5 grams = 6 grams

Sample 3 = feed 5 grams (no adsorbent)

Weight % of each component in sample 3 by Gas Chromatography method

1) hexene = 4.436 wt%

2) n-hexane = 4.361 wt%

3) i-octane = 91.203 wt%

y_e = mass of hexene at start

y_a = mass of hexane at start

y_i = mass of i-octane at start

y_e = $(6 * 4.436) / 100$ = 0.266 gram

y_a = $(6 * 4.361) / 100$ = 0.262 gram

y_o = $(6 * 91.203) / 100$ = 5.472 grams

1. Equilibrium Selectivity of Hexene/n-Hexane on NaX-zeolite (Sample 1)

x_i = mass of each component left in sample 1 after equilibrium adsorption

M_s = mass of each component in solution

M_a = mass of each component in adsorbent

Weight % of each component left in sample 1 by Gas Chromatography method

- 1) hexene = 2.761 wt%
- 2) n-hexane = 4.283 wt%
- 3) i-octane = 92.956 wt%

$$\begin{aligned}x_e &= \text{mass of hexene left in solution} \\&= (2.761/100)*M_s\end{aligned}\quad (A1)$$

$$\begin{aligned}x_a &= \text{mass of n-hexane left in solution} \\&= (4.283/100)*M_s\end{aligned}\quad (A2)$$

$$\begin{aligned}x_o &= \text{mass of i-octane left in solution} \\&= (92.956/100)*M_s\end{aligned}\quad (A3)$$

Mass of each component left in solution + Mass of each component in NaX-zeolite = $M_s + M_a = 6$ grams

$$(A4)$$

$$z_i = \text{Mass of each component in adsorbent}$$

$$z_e = y_e - x_e = 0.266 - x_e \quad (A5)$$

$$z_a = y_a - x_a = 0.262 - x_a \quad (A6)$$

$$z_o = y_o - x_o = 5.472 - x_o \quad (A7)$$

Assumption No I-octane (solvent) in adsorbent

$$\therefore z_o = 0 \text{ gram}$$

$$\text{Substitute } z_o \text{ in (A7)} \quad x_o = 5.472 \text{ grams}$$

$$\text{Substitute } x_o \text{ in (A3)} \quad M_s = (5.472 * 100) / 92.956 = 5.887 \text{ grams}$$

$$\text{Substitute } M_s \text{ in (A4)} \quad M_a = 6 - 5.887 = 0.114 \text{ gram}$$

$$\text{From (A1)} \quad x_e = (5.887 * 2.259) / 100 = 0.1625 \text{ gram}$$

$$\text{From (A2)} \quad x_a = (5.887 * 4.283) / 100 = 0.2521 \text{ gram}$$

$$\text{Substitute } x_e \text{ in (A5)} \quad z_e = 0.266 - 0.1625 = 0.1035 \text{ gram}$$

$$\text{Substitute } x_a \text{ in (A6)} \quad z_a = 0.262 - 0.2521 = 0.0099 \text{ gram}$$

To calculate equilibrium selectivity of hexene/n-hexane on NaX-zeolite adsorbent

$$\begin{aligned}
 \alpha (\text{hexene/n-hexane}) &= \frac{\frac{\text{mass of hexene in adsorbent}}{\text{mass of hexene left in solution}}}{\frac{\text{mass of n-hexane in adsorbent}}{\text{mass of n-hexane left in solution}}} \\
 &= \frac{(z_e/x_e)/(z_a/x_a)}{(0.1035/0.1625)/(0.0099/ 0.2521)} \\
 &= 16.23
 \end{aligned} \tag{A8}$$

2 Equilibrium Selectivity of Hexene/n-Hexane on Silicalite (Sample 2)

Weight % of each component in sample 3 by Gas Chromatography method is same as in case of NaX-zeolite.

$$\begin{aligned}
 x_i &= \text{mass of each component left in sample 1 after equilibrium adsorption} \\
 M_s &= \text{mass of each component in solution} \\
 M_a &= \text{mass of each component in adsorbent}
 \end{aligned}$$

Weight % of each component left in sample 2 by Gas Chromatography method

$$\begin{aligned}
 1) \text{ hexene} &= 4.041 \text{ wt\%} \\
 2) \text{ n-hexane} &= 4.002 \text{ wt\%} \\
 3) \text{ i-octane} &= 91.897 \text{ wt\%}
 \end{aligned}$$

x_e = mass of hexene left in solution

$$= (4.041/100) * M_s \tag{A9}$$

$$\begin{aligned}x_a &= \text{mass of n-hexane left in solution} \\&= (4.002/100)*M_s\end{aligned}\quad (\text{A10})$$

$$\begin{aligned}x_o &= \text{mass of i-octane left in solution} \\&= (91.897/100)*M_s\end{aligned}\quad (\text{A11})$$

Mass of each component left in solution + Mass of each component in Silicalite = $M_s + M_a = 6$ grams

$$\quad (\text{A12})$$

z_i = Mass of each component in adsorbent

$$z_e = y_e - x_e = 0.266 - x_e \quad (\text{A13})$$

$$z_a = y_a - x_a = 0.262 - x_a \quad (\text{A14})$$

$$z_o = y_o - x_o = 5.472 - x_o \quad (\text{A15})$$

Assumption No i-octane (solvent) in adsorbent.

$$\therefore z_o = 0 \text{ gram}$$

$$\text{Substitute } z_o \text{ in (A15)} \quad x_o = 5.472 \text{ grams}$$

$$\text{Substitute } x_o \text{ in (A11)} \quad M_s = (5.472 * 100) / 91.897 = 5.954 \text{ grams}$$

$$\text{Substitute } M_s \text{ in (A12)} \quad M_a = 6 - 5.954 = 0.046 \text{ gram}$$

$$\text{From (A9)} \quad x_e = (5.594 * 4.041) / 100 = 0.2406 \text{ gram}$$

$$\text{From (A10)} \quad x_a = (5.594 * 4.062) / 100 = 0.2419 \text{ gram}$$

$$\text{Substitute } x_e \text{ in (A13)} \quad z_e = 0.266 - 0.2406 = 0.0254 \text{ gram}$$

$$\text{Substitute } x_a \text{ in (A14)} \quad z_a = 0.262 - 0.2419 = 0.0201 \text{ gram}$$

To calculate equilibrium selectivity of hexene/n-hexane on silicalite adsorbent

$$\begin{aligned}\text{From (A8) } \alpha \text{ (hexene/n-hexane)} &= (z_e/x_e)/(z_a/x_a) \\&= (0.0254/0.2406)/(0.0201/0.2419) \\&= 1.27\end{aligned}$$

3. Equilibrium Selectivity of Hexene/n-Hexane on AgX-zeolite (Sample 4)

Feed 2 = 1 gram of n-hexane + 1 gram of hexene + 18 grams of i-octane = 20 grams

Sample 4 = 1 gram of AgX-zeolite + feed 5 grams = 6 grams

Sample 5 = feed 5 grams (no adsorbent)

Weight % of each component in sample 5 by Gas Chromatography method.

1) hexene = 3.837 wt%

2) n-hexane = 3.872 wt%

3) i-octane = 92.291 wt%

y_e = mass of hexene at start

y_a = mass of hexane at start

y_i = mass of i-octane at start

y_e = $(6 * 3.837) / 100$ = 0.2302 gram

y_a = $(6 * 3.872) / 100$ = 0.2323 gram

y_o = $(6 * 92.291) / 100$ = 5.5375 grams

x_i = mass of each component left in sample 4 after equilibrium adsorption

M_s = mass of each component in solution

M_a = mass of each component in adsorbent

Weight % of each component left in sample 4 by Gas Chromatography method

1) hexene = 1.966 wt%

2) n-hexane = 3.865 wt%

3) i-octane = 94.168 wt%

$$\begin{aligned}x_e &= \text{mass of hexene left in solution} \\&= (1.966/100)*M_s\end{aligned}\quad (A16)$$

$$\begin{aligned}x_a &= \text{mass of n-hexane left in solution} \\&= (3.865/100)*M_s\end{aligned}\quad (A17)$$

$$\begin{aligned}x_o &= \text{mass of i-octane left in solution} \\&= (94.168/100)*M_s\end{aligned}\quad (A18)$$

Mass of each component left in solution + Mass of each component in

$$AgX\text{-zeolite} = M_s + M_a = 6 \text{ grams} \quad (A19)$$

z_i = Mass of each component in adsorbent

$$z_e = y_e - x_e = 0.2302 - x_e \quad (A20)$$

$$z_a = y_a - x_a = 0.2323 - x_a \quad (A21)$$

$$z_o = y_o - x_o = 5.5375 - x_o \quad (A22)$$

Assumption No i-octane (solvent) in adsorbent.

$$\therefore z_o = 0 \text{ gram}$$

$$\text{Substitute } z_o \text{ in (A22)} \quad x_o = 5.5375 \text{ grams}$$

$$\text{Substitute } x_o \text{ in (A18)} \quad M_s = (5.5375 * 100) / 94.168 = 5.887 \text{ grams}$$

$$\text{Substitute } M_s \text{ in (A19)} \quad M_a = 6 - 5.887 = 0.113 \text{ gram}$$

$$\text{From (A16)} \quad x_e = (5.887 * 1.966) / 100 = 0.1157 \text{ gram}$$

$$\text{From (A17)} \quad x_a = (5.887 * 3.865) / 100 = 0.2275 \text{ gram}$$

$$\text{Substitute } x_e \text{ in (A20)} \quad z_e = 0.2302 - 0.1157 = 0.1145 \text{ gram}$$

$$\text{Substitute } x_a \text{ in (A21)} \quad z_a = 0.2323 - 0.2275 = 0.0048 \text{ gram}$$

To calculate equilibrium selectivity of hexene/n-hexane on AgX-zeolite adsorbent.

$$\begin{aligned}\text{From (A8)} \quad \alpha (\text{hexene/n-hexane}) &= (z_e/x_e)/(z_a/x_a) \\&= (0.1157/0.1145)/(0.0048/0.2275) \\&= 47.8926\end{aligned}$$

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