

4.2.7 Notation

- a = Energy parameter in Peng-Robinson equation of state [bar cm⁶/gmole²]
- a' = Peng-Robinson mixture parameter [bar cm⁶/gmole²]
- b = Size parameter in Peng-Robinson equation of state [cm³/gmole]
- c = Peng-Robinson mixture parameter [bar cm⁶/gmole²]
- d = Peng-Robinson mixture parameter [bar cm⁶/gmole²]
- d_p = Average diameter of sphere possessing the same surface area as a piece of packing [cm]
- D_v = Molecular diffusivity [cm²/sec]
- g = Gravitational acceleration [cm/sec²]
- G_f = Gibbs free energy
- Gr = Grashof number = $d_p^3 g \rho \Delta \rho / \mu^2$
- J_d = Mass transfer factor = $Sh Re^{-1} Sc^{-1/3}$
- K = Mixing expansivity
- k_{ij} = Binary interaction parameters
- k_y = Mass transfer coefficient [gmole/cm² sec mole-fraction]
- L_T = Total height of bed [cm]
- M = Molecular weight [g/gmole]
- n = Number of perfect mixers
- R = Gas constant = 83.14 [bar cm³/gmole °K]
- Re = Reynolds number = $\rho d_p u_g / \mu$
- S = Cross section area of packed bed [cm²]
- Sc = Schmidt number = $\mu / \rho D_v$
- Sh = Sherwood number = $k_c d_p / D_v$
- T = Absolute temperature [°K]
- \bar{V} = Partial molar volume of solute i [cm³/gmole]

- y = Mole fraction
 z = Compressibility factor
 \bar{z} = Change of compressibility factor with respect to the mole fraction at constant temperature and pressure

Greek Letters

- α_{ij} = Adjustable parameter
 β_{ij} = Adjustable parameter [cm^3/gmole]
 ϵ = Void fraction
 μ = Viscosity [g/cm sec]
 ρ = Density [g/cm^3]
 $\bar{\rho}$ = Density change with respect to the mole fraction at constant temperature and pressure [$\text{g/cm}^3\text{-mole fraction}$]
 ρ_{mol} = Molar density [gmole/cm^3]
 $\Delta\rho$ = Density difference between the fluid at the solid surface and the fluid in the bulk phase (CO_2 -naphthalene mixture)
 $\Delta\rho_{\text{pure}}$ = Density difference between the the fluid at the solid surface and the pure CO_2
 ξ = Chemical potential

Subscripts

- 1 = Solute component
 2 = Solvent component
 F = Forced convection
 m = Average properties
 N = Natural convection
 T = Total combined natural and forced convection

Superscripts

- = = Infinite dilution limit
- * = Equilibrium condition

4.3 Reference to Task 2

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4.4 Appendix to Task 4.2

PHYSICAL PROPERTIES

In addition to mass transfer coefficients, the development of mass transfer correlations needs knowledge of three physical properties: (1) viscosity of the SCF, (2) diffusion coefficient of the solute and (3) mixture density of the SCF phase.

4.4.1 Viscosity: In the present study the viscosity of the system is approximated as that of pure CO₂ (Stephan and Lucas, 1979). It is shown as a function of pressure as (Figure A-1) shown by by Chung et al. (Sherwood et al., 1975).

4.4.2 Diffusivity: At low to moderate pressures, diffusion coefficients vary inversely with pressure or density. Paulaitis et al. (1983) plotted diffusion coefficients as a function of reduced pressure of the solvents for the systems CO₂-naphthalene, CO₂ -benzene and ethylene-naphthalene, which showed D_V was inversely proportional to reduced pressure at low pressure (up to about $P_r = 0.5$; $P_c = 73.80$ bar for CO₂), but as the pressure approached the critical, this linearity was no longer true. Tsekhanskaya (1971) showed that the diffusion coefficient abruptly dropped to essentially zero near the lower critical end point (LCEP) where $T = 34.5^\circ\text{C}$, $P = 79.8$ bar, $y = 3.1 \times 10^{-4}$ and $\rho_{\text{CO}_2} = 0.47$ (Tsekhanskaya et al., 1962) and increased as the distance from this point increased. For low solubility systems, the LCEP is usually very close to the critical point of the solvent. The very small diffusivity near the LCEP can be explained by two points of view. The first is to assume that the diffusion in this region results from chemical potential gradients rather than concentration gradients. At the binary mixture critical point the second partial derivative of Gibbs free energy with respect to mole fraction is

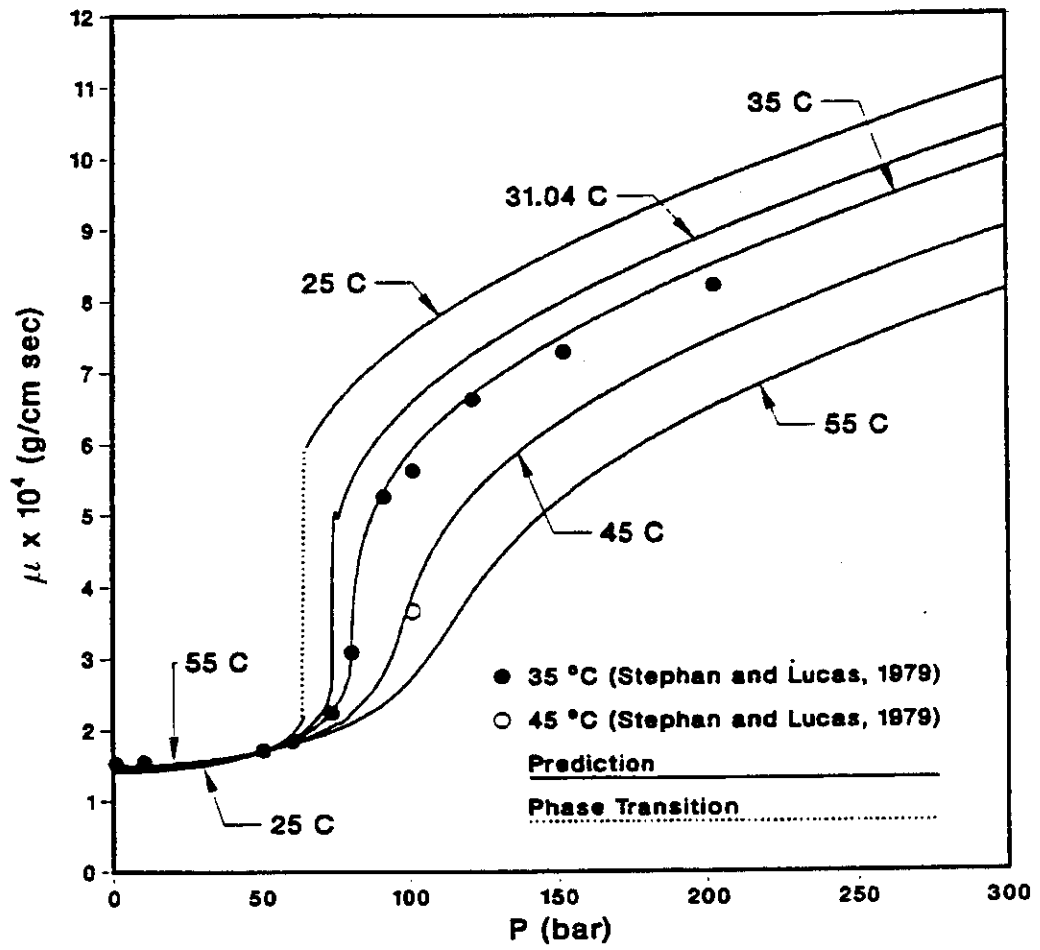


FIGURE A-1 Viscosity of Pure Carbon Dioxide

equal to zero for a stable phase ($\partial^2 G_f / \partial y_1^2 = 0$) and consequently the partial derivative of the chemical potential with respect to the mole fraction becomes zero ($\partial \mu / \partial y_1 = 0$). Therefore, the diffusion coefficient becomes zero and no diffusion occurs even though there is a finite concentration gradient. The second assumes that near the mixture critical point the diffusion process is controlled by the mobility of clustered molecules rather than single molecules which is common at normal conditions. As the pressure and temperature approach the mixture critical point, the size of clusters is dramatically increased (Debenedetti, 1987). The mobility of clusters decreases sharply with size resulting in an essentially zero diffusivity near the LCEP. The value of diffusivity near the LCEP is, however, very uncertain due to its extreme sensitivity to the temperatures and pressures (or densities). At 35°C and pressures up to 60.8 bar, we use the diffusivity interpolated from the experimental literature data (Morozov and Vinkler, 1975; Vinkler and Morozov, 1975) by assuming that D_v is inversely proportional to the density of CO₂.

$$\rho_{\text{CO}_2} D_v = 0.712546 \times 10^{-4} \text{ (g/cm-sec) at 35}^\circ\text{C and pressures up to 60.8 bar} \quad (\text{A-1})$$

Near the LCEP (35°C and 73.80-80.5 bar), we use the diffusivity interpolated from the experimental data obtained by Tsekhaskaya (1971) for the correlation given by equation (12). We use the equation below (A-2) for the correlation given by Equation (13). See the text for an explanation.

At pressures above the LCEP estimation of diffusion coefficients is more complex than below the LCEP. Even though no reliable correlation for diffusion coefficients at supercritical conditions has been developed, several

researchers (Swaid and Schneider, 1979; Feist and Schneider, 1982; Debenedetti, 1986) have shown a linear relationship between $\log D_V$ and ρ_{CO_2} at constant temperature in supercritical fluids. In the present study analytical relationships are determined for pressures above the critical using the experimental diffusion coefficient data for the CO_2 -naphthalene system presented by Iomtev and Tsekhanskaya (1964) at 35 and 45°C (Figure 6).

$$D_V = 4.2980 \times 10^{-4} \times 10^{8.8212 \rho_{CP_2}} \text{ (cm}^2\text{/sec) at 35}^\circ\text{C and 91.2-202.7 bar} \quad (\text{A-2})$$

$$D_V = 2.7290 \times 10^{-4} \times 10^{-0.5805 \rho_{CO_2}} \text{ (cm}^2\text{/sec) at 45}^\circ\text{C and 101.1 bar} \quad (\text{A-3})$$

The above equations, (A-2) and (A-3), are used to calculate diffusion coefficients at pressures above 91.2 bar at 35 and 45°C, respectively, in this study.

4.4.3 Density: The mixture densities of the CO_2 -naphthalene system are required at different compositions, temperatures and pressures. The mixture density is determined from the modified Peng-Robinson equation of state with temperature and density dependent binary interaction parameters, (Mohamed and Holder, 1987; Lim et al., 1988), and the average mixture density (ρ_m) for the experimental conditions is obtained by taking the arithmetic average of the three mixture densities at each cell. This average mixture density is used to calculate the average density differences ($\Delta\rho_m$) between the mixture fluid at the interface and the bulk. These average density and density difference were used to determine the values of dimensionless groups such as Re, Sc and Gr.

The standard form other P-R EOS (Peng and Robinson, 1976) is

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b) + b(V-b)} \quad (\text{A-4})$$

By considering both temperature and density effects on the binary interaction parameters, its standard form can be modified as:

$$k_{ij} = \alpha_{ij} + \beta_{ij} \rho_{\text{mol}} = \alpha_{ij} + \beta_{ij}/V \quad (\text{A-5})$$

Then, the modified P-R EOS becomes

$$P = \frac{RT}{V-b} - \frac{a' - c - d/V}{V(V+b) + b(V-b)} \quad (\text{A-6})$$

using the following mixing rule:

$$a' = \sum_i \sum_j y_i y_j \sqrt{a_i a_j}$$

$$b = \sum_i y_i b_i$$

$$c = \sum_i \sum_j y_i y_j \sqrt{a_i a_j} \alpha_{ij} \quad (\text{A-7})$$

$$d = \sum_i \sum_j y_i y_j \sqrt{a_i a_j} \beta_{ij}$$

$$\alpha_{ij} = \beta_{ij} = 0$$

At each temperature (35-55°C), two adjustable parameters α_{ij} and β_{ij} are optimized to minimize the percent absolute average relative deviation (% AARD) between the estimated solubilities and the experimental solubilities, the experimental solubilities obtained by Tsekhanskaya et al. (1964) and by McHugh and Paulaitis (1980) and Lim et al. (1989).

The densities of pure CO₂ are obtained from the literature (Angus et al., 1976) for the estimation of physical properties above. To get more accurate mixture densities, the mixture density calculated by the modified P-R EOS is corrected by the difference between the calculated pure CO₂ density and its literature value at the same temperature and pressure. Note that this correction cancels in estimating values of $\Delta\rho$.