

10.40 Thermodynamics  
Problem Set 10

Fall 2003

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Problem 15.38 Text

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**Solution:**

- (a) At equilibrium the fugacities of caffeine ( $i$ ) in the solid ( $S$ ) and supercritical fluid ( $f$ ) phase are equal.

$$\hat{f}_i^S = \hat{f}_i^f \quad (1)$$

Using the fugacity coefficient and Poynting correction to express either fugacity at a specific  $T$  and  $P$  and assuming that solid caffeine is pure. ( $x_i^S = 1$ ), then

$$\hat{f}_i^S \approx f_i^S = \phi_i^V(T, P_{vp,i}^{S-V}) P_{vp,i}^{S-V} \exp \left[ \int_{P_{vp,i}^{S-V}}^P \frac{V_i^S}{RT} dP \right] \quad (2)$$

$$\hat{f}_i^f = \hat{\phi}_i^f y_i^f P = \hat{\phi}_i^f(T, P, y_i) y_i^f P \quad (3)$$

Equating Eqs. (2) and (3) we can solve directly for the solubility ( $y_i^f$ ) in the supercritical  $\text{CO}_2$  phase.

$$y_i^f = \left[ \frac{P_{vp,i}^{S-V}}{P} \right] \left[ \frac{\phi_i^V(T, P_{vp,i}^{S-V})}{\hat{\phi}_i^f(T, P, y_i^f)} \right] \left[ \exp \left[ \int_{P_{vp,i}^{S-V}}^P \frac{V_i^S}{RT} dP \right] \right] \quad (4)$$

Given that the vapor pressure of solid caffeine is low,  $\phi_i^V(T, P_{vp,i}^{S-V}) \approx 1.0$

- (b) In Problem 13.4, we estimated critical constants and  $\omega$  for pure caffeine using molecular group contributions. Thus, we can use the PR EOS written for the binary  $\text{CO}_2$ -caffeine mixture to estimate  $\hat{\phi}_i^f(T, P, y_i^f)$ . The other information provided in the problem statement allows us to estimate

$$V_i^S = (1/\rho_i^S) 194.2 = 6.334 \times 10^3 \text{ m}^3/\text{mol}$$

$$\log_{10} P_{vp,i}^{(S-V)} = -5781/T + 15.031$$

The PR EOS form for  $\hat{\phi}_i^f$  is given Chapter 9 by Eq. (9-144) using the standard mixing rules that apply to the PR EOS given by Eqs. (9-27) – (9-30). A FORTRAN code was written to solve for  $y_i^f$  (Eq. (4)) using the PR EOS to estimate  $\hat{\phi}_i^f$  for assumed values of  $y_i^f$  at specific values of  $T$  and  $P$ . This involved an iterative approach with the sum of squared errors (SSE) between experimental and predicted  $y_i$  used as an objective function to find an optimal binary interaction parameter  $\delta_{ij}$ , where

$$SSE = \Phi_{objective} = \sum_i \left[ (y_{i,exp} - y_{i,predicted}) / y_{i,exp} \right]^2$$

At 60°C. for pressures ranging from 150 to 330 bar,  $\Phi$  was minimized by selecting  $\delta_{ij}$ . Results follow for the following specific set of critical constants and  $\omega$  for caffeine derived using the group contribution methods of Chapter 13, e.g., see Problem 13.4.

$$T_c = 872 \text{ K}$$

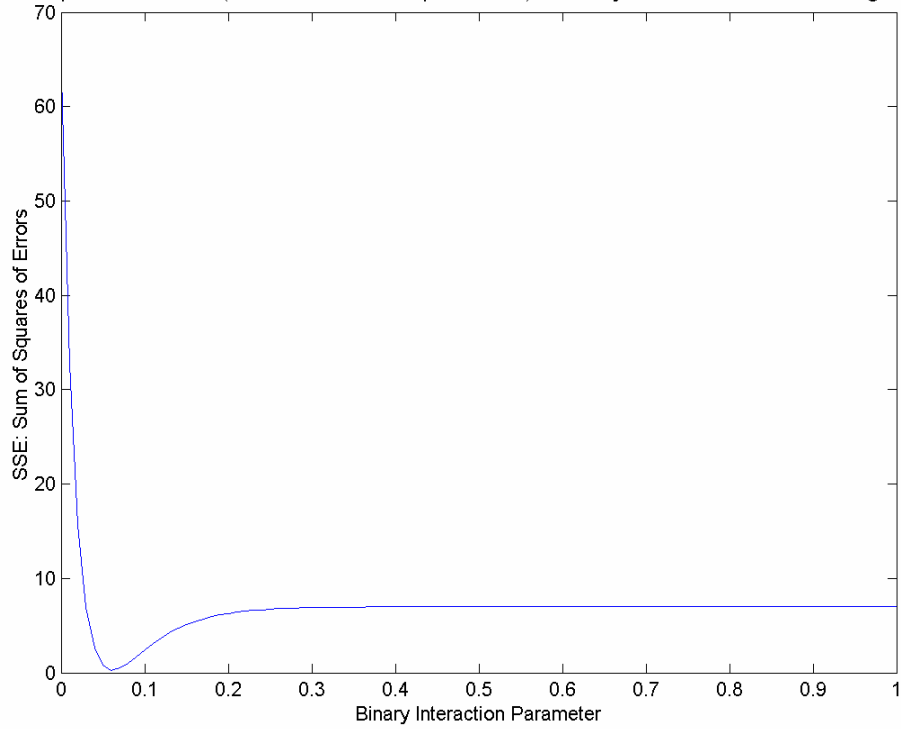
$$P_c = 41.5 \text{ bar}$$

$$\omega = 0.898$$

The optimal  $\delta_{ij} = k_{ij}$  was found to be 0.059 where excellent agreement between experimental and predicted solubilities was observed. As an alternative to the FORTRAN code, MATHEMATICA or MAPLE could be used to iterate on  $y_i^f$  in Eq. (4) and to locate an optimal  $\delta_{ij}$ .

If an accentric factor of  $\omega = 0.908$  that was found using our approach in Problem 3, then the optimal  $\delta_{ij} = k_{ij}$  was found to be 0.061. This is almost the same as the previous result. The following graphs show how the sum of the square of the errors varies with the binary interaction parameter, and also shows where the sum of errors is minimized. The final figure shows how the mole fraction of caffeine varies with pressure for the optimized binary interaction parameter. The curve is in excellent agreement with the experimental data points.

Sum of the Squares of the Error (Difference between Exp. and Calc.) vs. Binary Interaction Potential for Peng-Robinson EC



Sum of the Squares of the Error (Difference between Exp. and Calc.) vs. Binary Interaction Potential for Peng-Robinson EC

