Caffeine Extraction Rates from Coffee Beans with Supercritical Carbon Dioxide

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The extraction of caffeine from whole coffee beans with supercritical carbon dioxide was studied in a continuous-flow extraction apparatus. Decaffeination rates were determined as a function of CO_2 flow rate, temperature and pressure by continuously monitoring the caffeine in the effluent with a flame ionization detector. Soaking the raw beans in water prior to decaffeination enhanced the rate of extraction, which increased markedly with water content. Using CO_2 saturated with water also increased the rate of extraction. The rate of decaffeination increased with pressure and temperature and was influenced by both intraparticle diffusion in the water-soaked beans and external mass transfer. A mathematical model based on a linear-driving-force approximation of mass transfer and partitioning of caffeine between the water and the supercritical CO_2 describes the time-dependent process. The partition coefficient for caffeine distributed between water and supercritical CO_2, the only parameter determined from the dynamic extraction rate data, increases with temperature and pressure.

Introduction

Decaffeination of coffee beans has been carried out with a variety of conventional solvents such as dichloromethane (Stahl et al., 1988; McHugh and Krukonis, 1986), but recently supercritical CO_2 has been the preferred solvent in large-scale commercial processes (Leyers et al., 1991). The selectivity of supercritical CO_2 for caffeine in green (unroasted) coffee beans is an important property that is exploited in the decaffeination process, as little else besides caffeine in the raw bean is thought to be soluble in supercritical CO_2 (Stahl et al., 1988). Since extraction is performed on the raw beans, flavor ingredients that are developed only during roasting are not removed. Additionally, use of supercritical CO_2 precludes any post-decaffeination treatment of the beans to remove the solvent, a necessary step if conventional organic solvents are used.

This supercritical fluid process is representative of a wide range of possible extractions: (a) to remove unwanted chemicals from the desired matrix material or (b) to separate and isolate a desired chemical from the matrix. A fundamental understanding is needed of the chemical, physical and transport processes that affect such extractions. The aim of the present research is to develop general experimental and theoretical approaches to study these basic phenomena as well as the particular decaffeination process.

Supercritical CO_2 extraction, including the patents for caffeine extraction, is discussed by McHugh and Krukonis (1986) and Paulaitis et al. (1983). Stahl et al. (1988) also provide useful information about the decaffeination of raw coffee beans, which may contain 0.6 to 3 wt % of caffeine. The beans are first soaked in water up to a water content of 45 wt. %. Essential for satisfactory extraction, this step may change the texture of the cell walls to enhance diffusion, which is considered a rate-determining step, or the water may free the bound caffeine from the coffee matrix (McHugh and Krukonis, 1986).

Udayasankar et al. (1986) extracted caffeine from coffee beans with supercritical CO_2 in a batch mode. Prior to extraction the beans were moistened with saturated steam to achieve 40 wt. % water. Data for caffeine content as a function of extraction time were used to estimate a diffusion coefficient of caffeine from the beans based on a diffusion model for extraction. Brunner (1984, 1985) used a commerical apparatus to extract coffee beans with nitrous oxide, N_2O. Results from the continuous-flow apparatus showed that for intermediate extraction times, the rate increased with flow rate. Brunner also suggested that mass-transfer resistance in the bean dominates in supercritical decaffeination. Based on a concentration driving-force model, he calculated values of the mass-transfer coefficient that allowed good agreement with experimental data for the amount extracted. To simplify the computations the model included approximate assumptions that caffeine concentration at the mass-transfer interface is constant and that concentration at the bed outlet is 90% of the equilibrium concentration. In the case where a mixture of CO_2 and N_2O was used as the solvent medium (Brunner, 1988), the gas-flow rate was found to be an important parameter.

Srinivasan et al. (1990) and Goto et al. (1990) investigated supercritical extractions that were controlled by mass-transfer or chemical reaction. The experimental equipment for the continuous-flow studies utilized a small (differential) bed of solid particles and continuous monitoring of the effluent solvent. The extract concentration histories allowed discrimination between alternative models that included intraparticle diffusion, external mass transfer, adsorption-desorption rates, and chemical reaction mechanisms.

The objective of this article is to study extraction of caffeine from coffee beans in a manner similar to that employed by Srinivasan et al. (1990) for the desorption of ethyl acetate from activated carbon. This method employs a flame ionization detector (FID) to measure continuously the combustible material in the effluent. Our data confirm that monitoring the effluent for the continuous flow of solvent through a differential bed of particles (seven coffee beans) provides detailed information (concentration histories) needed for developing and testing a mathematical model. Conventional monitoring techniques, such as measurement of cumulative concentration of extract collected in a solvent trap, yield plots of cumulative fraction extracted (integrated over concentration history) vs. time. In our previous attempts to reconcile experimental and theoretical data (Srinivasan et al., 1990), we found that, compared to integrated cumulative data, concentration-history data facilitated discrimination between theoretical models. In the present case, the diffusion and mass-transfer parameters are estimated from literature data and correlations, and a single parameter, the partition coefficient, is determined from the experimental data at various values of temperature and pressure.

Experiments

Experimental apparatus

The experimental apparatus shown in Figure 1 is similar to that described in detail by Srinivasan et al. (1990). Liquid CO_2 from a cylinder with siphon attachment is fed to a piston accumulator that is driven by high-pressure N_2. The N_2 is prevented from contaminating the CO_2 by O-rings on the piston. The extraction column (Autoclave Engineers, Inc.), 1.27 cm in height and 1.73 cm in diameter, contains a bed of seven coffee beans sandwiched between sieves. Compressed CO_2 flows to the extraction column immersed in a constant-temperature water bath that maintains the operating temperature within ±0.1°C.

Part of the effluent from the column is metered to the flame ionization detector. The volumetric flow rate (at ambient temperature and pressure) of this side stream, which measures the concentration of combustible gases, is maintained constant, while the variable remainder is expanded to ambient pressure and vented through a rotameter. The FID (GowMac) is designed so that the fluid is supercritical up to the nozzle exit, where the fluid jets directly into the flame. The FID and the metering valve are maintained at 200°C in an oven. The FID provides continuous, distortion-free data for the column effluent concentration, since the effluent is in the supercritical phase up to the instant of detection. Presence of organics in the effluent is detected by means of a pair of electrodes in the FID coupled to a sensitive electrometer, the latter in turn connected to a chart recorder. The response recorded on the chart

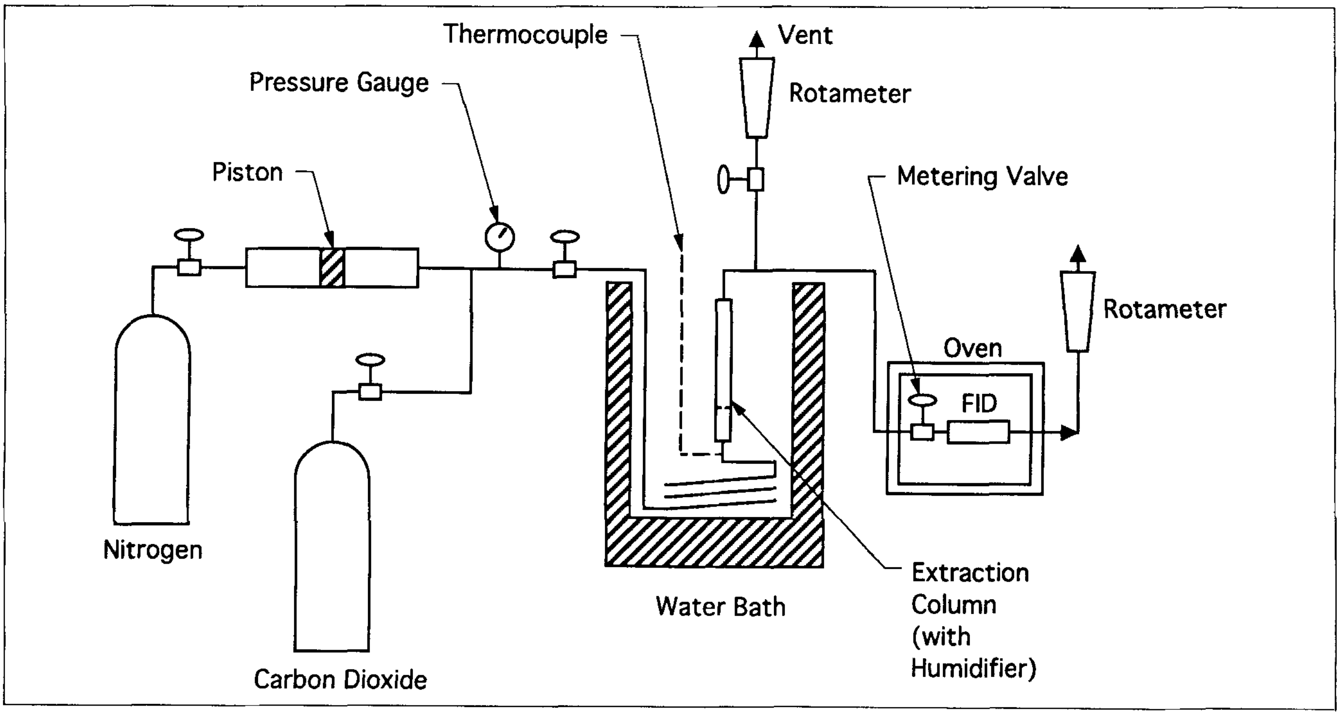

Figure 1. Experimental apparatus for supercritical CO_2 decaffeination of coffee beans.

is proportional to the concentration of combustible organics in the effluent stream.

Calibration of the FID is achieved from integrated signal responses after introduction of a standardized mass of pure caffeine (Sigma Chemical Co.) into the chromatographic system. A calibration curve is obtained by relating the mass of sample to the concentration of the standard, the flow rate of the chromatographic system, and the limits of time from the start to the end of detection ($M=\int_o^t cQdt$). This calibration process is the same as relating the mass of the standard to the peak area of the signal ($M=N\times$ area), where N is a proportionality constant equal to 1.18×10^{-6} g/cm^2. The volumetric flow rate (Q) through the detector is constant for all analyses. Based on these equations, concentration is determined as $c=zN/Q$, where z is the measured signal. To obtain data points from the continuous recorder printout, the average reading in every 2.5 minute interval was noted. For concentration history plots, every other data point was plotted. For cumulative fraction plots, the points at 2.5-min intervals were integrated by Simpson's rule, and every fourth point was plotted.

Experimental procedure

Initially, the FID is ignited, and the water bath holding the column is brought to the operating temperature. CO_2, and then N_2, are fed to either side of the piston in the piston accumulator, and pressure on the N_2 side is adjusted to the operating pressure. CO_2 held in the accumulator is compressed to the operating pressure. The seven coffee beans, held between screens, are positioned in the extraction column, which is then immersed in the water bath. The metering valves are adjusted to the desired flow rates, and the CO_2 at operating pressure is allowed to flow through the extraction column. At the end of the run, the CO_2 flow is stopped, the column is depressurized, and the beans are removed from the column. To determine the reproducibility of concentration-time histories, extraction runs were conducted with the same extraction conditions for different sets of beans of approximately the same weight.

Preliminary experiments

To determine if caffeine was the only measurable substance present in the effluent, a preliminary extraction with raw coffee beans was performed, in which the effluent was bubbled separately through warm water and ethanol. With a UV-VIS spectrophotometer (Perkin Elmer), the resulting solutions were compared to made-up solutions of pure caffeine in water and in ethanol. The scans over a range of wavelength were nearly identical, suggesting that only caffeine or caffeine-like compounds were present in the effluent in detectable quantities.

To obtain an estimate for the initial concentration of caffeine in the raw beans, an extraction run was continued to extinction, ensuring that all extractable material had been removed. The amount of caffeine thus extracted was calculated from the response of the FID and was used to obtain the initial concentration. The mass of caffeine (per mass of dry bean) was multiplied by the mass of dry bean and divided by the volume of a water-soaked bean to obtain the initial intraparticle concentration, c_o (g caffeine/cm^3 wet bean). As mentioned below, this value of c_o is larger than most specific analyses of caffeine content found in the literature. Even though the process may extract small amounts of compounds other than caffeine, based on the available evidence, we consider that the extracted material has properties similar to those of caffeine.

Effect of moisture

To study the effect of moisture on extraction, the raw coffee beans were contacted with distilled water at room temperature in a mechanical shaker for times ranging from 0.5 to 24 hours. The soaked beans were dried with paper towels and weighed to determine weight increase due to absorption of water. Extraction was carried out with raw unsoaked beans that were dried at 80°C for 4 hours and with beans soaked from 0.5 hours up to 24 hours. The conditions of extraction were 323 K, 136 atm (13.8 MPa), and a flow rate for CO_2 of 1.51 mL/min at column conditions (Figure 2).

The weight of the beans before and after extraction indicated that water was being removed from the beans. Since water facilitates the extraction process (Stahl et al., 1988), loss of moisture from the bean during extraction causes a decreasing rate of extraction with time. To prevent loss of moisture, the supercritical CO_2 stream was contacted with calcium sulfate (Drierite) laden with enough water to humidify the supercritical CO_2 throughout the duration of the run. The small amount of water in the supercritical CO_2 (less than 1%) acts as a cosolvent for the extraction. The bed of calcium sulfate was placed in the extraction column 10 cm upstream of the bed of coffee beans. While the weight loss of the beans with dry CO_2 was about 50%, the loss using the humidified CO_2 was only about 5%. The flow rate, pressure and temperature effects were studied with the humidified supercritical CO_2.

Effect of flow rate, pressure and temperature

The effect of flow rate was studied by holding the pressure and temperature at 136 atm (13.8 MPa) and 323 K, respectively, and varying the flow rate. For all the runs, the raw beans were contacted with water in the mechanical shaker for a period of 12 hours, prior to loading into the column. According to Figure 2, this pretreatment resulted in an initial water content of 41.4%. The flow rates of CO_2 employed were 0.682, 1.51, 2.44 and 4.59 mL/min at column conditions. Densities of CO_2 were determined by a Peng-Robinson equation of state. The volumetric flow rate 2.44 mL/min corresponds to the mass-flow rate 1.51 g/min. For studying the effect of pressure, extractions

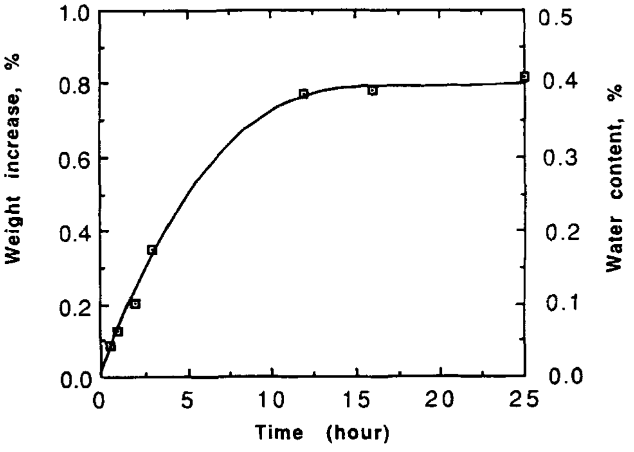

Figure 2. Weight increase and % water content of coffee beans vs. time of soaking.

were conducted at a temperature of 323 K, a mass-flow rate of 1.51 g/min, and four different pressures: 10.3, 13.8, 16.5 and 19.3 MPa ($P_r = 1.38$ to 2.58). For the temperature effect, pressure and mass-flow rate were held at 13.8 MPa and 1.51 g/min, respectively, and temperature for the four runs were set at 313, 323, 337, and 353 K ($T_r = 1.03$ to 1.17).

Mathematical Model

It is postulated that extraction from the water-soaked bean occurs by the caffeine desorbing from the solid biotissue, dissolving in the water and diffusing to the external surface of the beans and through the boundary layer to be carried away by the supercritical CO_2. The rate of the overall process can be influenced by caffeine desorption from the tissue into the water, the partitioning between the water and supercritical CO_2, and the mass-transfer process, including intraparticle diffusion and external mass transfer.

We assume that the differential bed is approximated by a gradientless volume of beans and fluid, which allows the convective term to be written as c/τ, where the time τ is the total bed volume divided by the volumetric flow rate of supercritical fluid. The partitioning of the caffeine between the CO_2 and the water in a bean is given by the partition coefficient, m, defined as the ratio of the caffeine concentration in the supercritical CO_2 to that in water at equilibrium. We also consider that initially the caffeine is uniformly distributed throughout the beans, which are approximated as spheres of an equivalent radius.

It is assumed that the combined internal and external mass-transfer processes are described by a linear driving-force model (Srinivasan et al., 1990) with overall mass-transfer coefficient given by Eq. A11, $k_p = (15\,k_f/R)/(5 + mBi)$, in which k_f is the external film mass-transfer coefficient and R is the bean radius (for an equivalent sphere). A derivation and discussion are provided in the Appendix for the linear driving-force model, which is known to be accurate except for a brief initial time (Do and Rice, 1986). The Biot number, $Bi = k_f R/D_e$, is expressed in terms of the effective intraparticle diffusion coefficient, D_e. When $Bi \gg 5/m$ intraparticle diffusion resistance would dominate over the external mass-transfer resistance.

With this model the governing differential equation for the time-dependent caffeine concentration in the CO_2 in the voids, $c(t)$, in the differential bed of beans is:

$$\alpha dc/dt + c/\tau = -(1-\alpha)a_p k_p{}'\,(c - mc_i) \tag{1}$$

where α is the bed void fraction and the overall mass-transfer coefficient is $k_p = k_p{}'\,a_p$ in terms of $a_p = 3/R$. The mass balance for the intraparticle caffeine concentration, $c_i(t)$, in terms of the bean porosity β is:

$$\beta dc_i/dt = k_p{}'\,a_p(c - mc_i) - (1-\beta)dc_s/dt \tag{2}$$

For $m = 1$, these equations reduce to the case of extraction from dry matrix material.

Next, an expression for the rate of desorption, $-dc_s/dt$, is required. If the desorption process is reversible and linear, then the rate of adsorption is given by:

$$dc_s/dt = k_a(c_i - c_s/K) \tag{3}$$

in terms of the adsorption rate constant k_a and the equilibrium adsorption coefficient K. For a relatively fast adsorption-desorption rate (large value of k_a), the adsorption equilibrium condition holds,

$$c_s = K\,c_i \tag{4}$$

from which we have

$$dc_s/dt = K\,dc_i/dt \tag{5}$$

Under the adsorption equilibrium condition, Eq. 5 applies instead of Eq. 3. Analysis of our data indicates that when the coffee beans are initially thoroughly saturated with water (after 12-h soaking time), the rate expression, Eq. 3, is not needed.

At the beginning of the supercritical run, the caffeine is inside the coffee bean and distributed between the adsorbed and desorbed states. For the case of adsorption equilibrium, the total caffeine concentration is:

$$c_o = \beta c_{io} + (1-\beta)kc_{io} \tag{6}$$

Dimensionless quantities are defined as follows:

$$x = c/c_o \tag{7}$$

$$y = c_i/c_o \tag{8}$$

$$\theta = \mathrm{t}/\tau \tag{9}$$

$$\phi = k_p{}'\,a_p\tau \tag{10}$$

When adsorption equilibrium is assumed, Eq. 5 can be used to eliminate c_s from Eq. 2. Then writing Eqs. 1 and 2 in dimensionless form yields:

$$dx/d\theta + x/\alpha = -\phi(x - my)(1-\alpha)/\alpha \tag{11}$$

$$dy/d\theta = \phi(x - my)/[\beta + (1-\beta)K] \tag{12}$$

Initial conditions are

$$x(\theta = 0) = 0 \tag{13}$$

and

$$y(\theta = 0) = 1/[\beta + (1-\beta)K] \tag{14}$$

The solution to Eqs. 11-14 is:

$$x(\theta) = A\exp(a_1\theta) + B\exp(a_2\theta) \tag{15}$$

where

$$a_1 = [-b + (b^2 - 4c)^{1/2}]/2 \tag{16}$$

$$a_2 = [-b - (b^2 - 4c)^{1/2}]/2 \tag{17}$$

$$A = -B = (1-\alpha)m\phi/\{[\beta + (1-\beta)K]\alpha(a_1 - a_2)\} \tag{18}$$

The parameters b and c are defined as:

$$b = m\phi/[\beta + (1-\beta)K] + 1/\alpha + \phi(1-\alpha)/\alpha \tag{19}$$

and

$$c = m\phi/[\beta + (1-\beta)K\alpha] \tag{20}$$

The form of the solution is such that ϕ and $m\phi/[\beta + (1-\beta)K]\alpha$ appear as two separate dimensionless groups. Thus, the decaffeination data as concentration histories cannot provide separate values of m and K. For $K \ll 1$, the caffeine essentially would be totally desorbed from the bean tissue into the water in the pores. As discussed below, enough water is present in the water-saturated coffee beans to desorb (dissolve) all the caffeine. Furthermore, the values of m calculated for $K \ll 1$ are consistent with values of m reported in the literature. Thus, we assume in the following analysis of the data that $K \ll 1$, so that initially all the caffeine is desorbed and in solution within the beans.

The solution, Eq. 15, consists of two exponentials with negative coefficients a_1 and a_2, one of which, a_1, is smaller and dominates the behavior at large values of time. At very small times, when the concentration of caffeine in the effluent is rapidly increasing, the experimental data are not precise enough to allow determination of parameters. This suggests that to analyze the experimental data, a plot of ln (x) vs. θ should provide a straight line for all but small values of θ. The slope of this line is a_1 and the intercept is ln (A). Values of a_1 and A determined from the data in this manner are used to solve for m, the principal parameter in the model. Terms appearing in the expression for the mass-transfer parameter ϕ are estimated from literature data. Only one parameter, the partition coefficient, m, is determined from the experimental data. For testing the model with Eq. 15, the data employed were from the runs (with beans soaked for 12 h and with humidified CO_2), showing the effects of flow rate, pressure and temperature.

The model has some similarities to the approximate extraction model proposed by Bartle et al. (1990), which is based on the long-time approximation of the solution to the diffusion equation for a sphere. Bartle et al. also found a simple exponential decay of extract concentration for the extraction from dry matrix material.

The cumulative fraction of caffeine extracted up to dimensionless time θ is defined in terms of the integral of x:

$$F(\theta) = (1/(1-\alpha))\int_0^\theta x\,d\theta = [1/(1-\alpha)]\{[\exp(a_1\theta) - 1] \times A/a_1 + [\exp(a_2\theta) - 1]B/a_2\} \tag{21}$$

and approaches unity at large values of time.

Results and Discussion

Effect of soaking time

Figure 2 shows that after an initial rapid increase in weight with time of soaking, the weight of the beans increased to a steady value at about 12 hours, which was chosen as the soaking time for the extraction runs. The supernatant water, analyzed spectrophotometrically by wavelength scanning, contained a negligibly small amount of caffeine. The beans are swollen after soaking, and the observed increase in volume for a bean corresponds to the increase in weight caused by uptake of water. The beans appear blanched after contact with water for long times, and the water acquired a slight greenish tinge, presumably due to loss of pigments from the bean. For four trials, the average weight of one coffee bean before and after 12 hours of soaking in water was 0.171 g and 0.303 g, respectively. Thus, on average, 0.132 g of water per bean, or 41 wt. % was absorbed during the 12-h soaking procedure. At 323 K, the solubility of caffeine in water is 6.3% (Sivetz and Desrosier, 1979), which is sufficient to dissolve all of the caffeine.

Table 1 provides information about size, density and porosity of dry and water-soaked beans. Coffee beans were considered to be half ellipsoids with semi-axial lengths a_o, b_o, and c_o; the average dimensions of wet and dry beans (20 samples of each) were measured and are reported in Table 1. The volume is given by $(1/2)(4/3)\pi a_o b_o c_o$, and the radius of the sphere of equivalent volume is R. Based on the above data, the densities of the dry and wet bean can be computed. The density of the solid material within the dry bean, calculated with the dry bean porosity (0.10), was 1.37 g/cm^3. The dry bean porosity was determined with a helium pycnometer. The wet bean porosity, $\beta = 0.515$, the volume fraction filled with water, was computed from the data. Since the bed volume is 2.98 cm^3, the bed void fraction is given by $\alpha = 0.371$.

To check reproducibility, two runs were done at each experimental condition. The maximum deviation between each run was less than ±10%, except for the highest T and P, where the deviations were considerably larger. The estimates of m determined at these conditions of highest temperature and pressure are judged less reliable than the other values of m.

The initial concentration of extractable caffeine was 0.038 g caffeine/g dry bean or 0.0242 g caffeine/cm^3 wet bean, determined as described earlier by extracting beans to completion and monitoring the effluent with the nonspecific detector. The value $c_o = 0.038$ g caffeine/g dry bean is larger than reported values based on specific quantitative analysis for caffeine. The largest reported value for caffeine content (dry-bean basis) is 3% (Stahl et al., 1988). It is widely believed that decaffeination by supercritical CO_2 extraction is highly, or even exclusively, selective for caffeine. Our study suggests, however, that compounds other than caffeine may be extracted, although they have properties similar to those of caffeine. The *uv* absorbance spectra of the extract and pure caffeine in water are essentially identical.

Table 1. Properties of Dry and Water-Soaked Coffee Beans

	a_o cm	b_o cm	c_o cm	R cm	V cm^3	ρ g/cm^3	ρ_{solid} g/cm^3	β
Dry Bean	0.506	0.340	0.386	0.321	0.139	1.233	1.370	0.100
Wet Bean	0.601	0.415	0.513	0.400	0.268	1.180	1.370	0.515

Table 2. Flow Rate Effect on Parameters

Flow Rate cm^3/min	u cm/s	τ min	Re	Sc	Bi	k_f cm/s	k_p 1/s	m	ϕ
0.682	0.0048	4.37	4.06	5.56	421	0.00139	0.0076	0.0045	1.99
1.51	0.0107	1.97	8.99	5.56	600	0.00198	0.0091	0.0053	1.07
2.46	0.0174	1.21	14.63	5.56	760	0.00251	0.0122	0.0036	0.89
4.59	0.0326	0.65	27.40	5.56	1,050	0.00347	0.0132	0.0047	0.51

All properties are for $P = 13.8$ MPa and 323 K.
$\alpha = 0.371$; $\beta = 0.515$; $\rho = 0.617$ g/cm^3; $\mu = 0.0005873$ g/cm·s; $D_e = 1.32 \times 10^{-6}$ cm^2/s.

Table 3. Temperature Effect on Parameters at $P = 13.8$ MPa

T K	D_{ab} cm^2/s × 10^4	D_e cm^2/s × 10^6	ρ g/cm^3	μ g/cm·s × 10^4	u cm/s	τ min	ϕ
313	1.32	1.05	0.720	7.34	0.0149	1.413	1.07
323	1.71	1.32	0.617	5.87	0.0174	1.211	0.88
337	2.13	1.76	0.474	3.82	0.0227	0.930	0.68
353	2.72	2.39	0.365	1.48	0.0294	0.717	0.36

T K	Re	Sc	Bi	k_f cm/s	k_p 1/s	m
313	11.7	7.72	724	0.0019	0.0126	0.00089
323	14.6	5.56	758	0.0025	0.0121	0.0036
337	22.5	3.77	795	0.0035	0.0122	0.0073
353	58.2	1.49	937	0.0056	0.0083	0.021

Properties of supercritical CO_2 at the operating conditions are listed in Tables 2-4. The caffeine-CO_2 binary diffusion coefficients for supercritical conditions, estimated by the method of Takahashi (Reid et al., 1987), were based on low-pressure values from the Fuller equation (Reid et al., 1987). Supercritical CO_2 densities and viscosities were estimated by the Peng-Robinson equation of state and the method of Tan and Liou (1988), respectively. The external mass-transfer coefficient k_f was computed with the Wakao and Kaguei (1985) correlation.

The effective intraparticle diffusion coefficient for caffeine in the water-soaked bean (Tables 2-4) is D_e, values of which are given by Bichsel et al. (1976). The value of D_e at 323 K is determined to be 1.32×10^{-6} cm^2/s, which can be compared to 2.32×10^{-6} cm^2/s if estimated by the formula $D_e = D\beta^2$. The binary diffusion coefficient for caffeine in water is $D = 5.31 \times 10^{-6}$ cm^2/s at 294.5 K and 1 atm (Bichsel et al., 1976). Values of D_e are corrected for temperature by a method given by Reid et al. (1987). Owing to the low diffusivity of caffeine in water-soaked beans, the Biot number is much greater than 5; however, due to the presence of the small-valued partition coefficient m in the denominator of Eq. A11, the intraparticle and external mass-transfer processes both contribute to the mass-transfer effect.

Two extraction runs were conducted at the same experimental conditions: one with dry CO_2 and the other with humidified supercritical CO_2. The concentration histories at small times showed little difference between the two runs. Overall, however, the concentration and hence the rate of extraction were greater for the humidified CO_2. This result suggests that *the initial rate of extraction is maintained for the dry* CO_2 *until* enough moisture is lost to the CO_2 to cause a decrease in the rate of extraction, while the higher rate is maintained for all times in the case of the humidified CO_2.

Figure 3, showing the effect of soaking time on extraction, is a plot of effluent concentration (caffeine in CO_2) as a func-

Table 4. Pressure Effect on Parameters at $T = 323$ K

P MPa	D_{ab} cm^2/s × 10^4	D_e cm^2/s × 10^6	ρ g/cm^3	μ g/cm·s × 10^4	u cm/s	τ min	ϕ
10.3	2.34	1.32	0.409	3.75	0.0262	0.802	1.08
13.8	1.71	1.32	0.617	5.87	0.0174	1.211	0.88
16.5	1.58	1.32	0.697	7.57	0.0155	1.368	0.79
19.3	1.19	1.32	0.752	9.27	0.0143	1.475	0.35

P MPa	Re	Sc	Bi	k_f cm/s	k_p 1/s	m
10.3	22.8	3.92	1,180	0.0039	0.0224	0.0013
13.8	14.6	5.56	758	0.0025	0.0121	0.0036
16.5	11.4	6.88	667	0.0022	0.0096	0.0054
19.3	9.3	10.36	515	0.0017	0.0040	0.0215

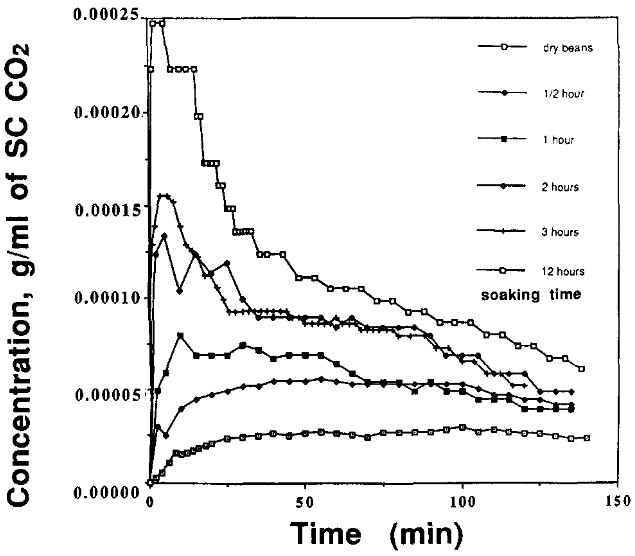

Figure 3. Effect of water content (soaking time) on caffeine extraction.

tion of extraction time. As these experiments were conducted at the same temperature, pressure and flow rate, the effluent concentration is a measure of the extraction rate. There is a noticeable increase in the concentration levels for the soaked beans compared to the level for the dry beans. This increase is in agreement with earlier studies where moisture was introduced either by soaking the beans or by using moist CO_2 (McHugh and Krukonis, 1986). For dry beans, the extraction is very low. The explanation, consistent with our mathematical model, is that insufficient water is available to desorb all the caffeine unless the beans are water-saturated.

Effect of flow rate

The effect of flow rate is described by means of the concentration history or by the cumulative fraction extracted. Figures 4 and 5 show the experimental results as plots of the histories of the effluent concentration and cumulative fractions at different flow rates, respectively. The concentrations increase rapidly from zero and then decrease gradually (Figure 4). The cumulative fractions approach 1.0 at long times (Figure 5). The concentration histories and cumulative fractions for lower flow rates indicate a need for long extraction times at these conditions. Values of m were determined from the best fit of the slope, a_1, and intercept, A, of ln x vs. θ at large values of θ. Table 2 shows values of the partition coefficient m at the four flow rates; the average of the four values is 0.0044 ± 0.0007. Since m should not depend on the flow rate, 16% standard deviation from the mean value is an indication of the error in the estimate of m based on long-time dynamic extraction data.

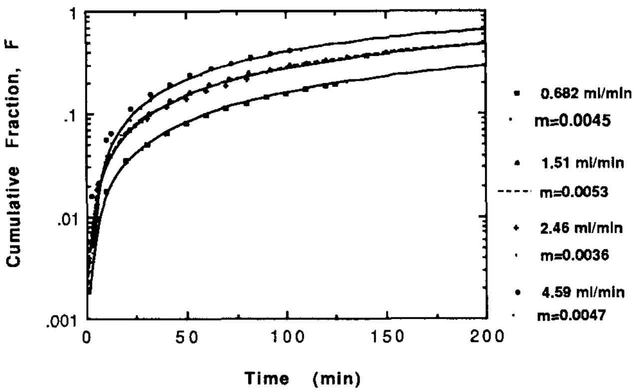

Figure 5. Effect of CO_2 flow rate on cumulative fraction of caffeine extracted vs. time at 13.8 MPa and 323 K.

Points represent experimental data; lines are predicted results.

Effect of pressure and temperature

The effects of pressure and temperature are shown in Figures 6-9. For a constant flow rate, the dimensionless concentration x is proportional to the rate of extraction. Hence, Figures 6 and 8 indicate that the rate of extraction increases with both pressure and temperature. The proposed model gave values of

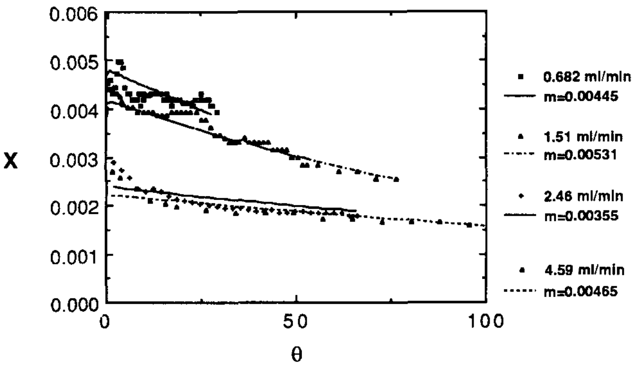

Figure 4. Effect of CO_2 flow rate on concentration histories of extracted caffeine at 13.8 MPa and 323 K.

Points represent experimental data; lines are predicted results.

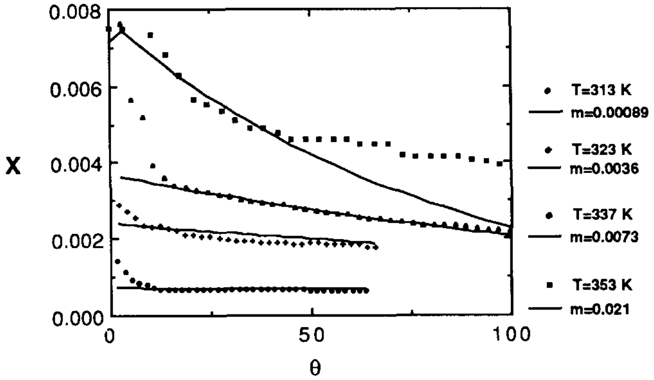

Figure 6. Effect of temperature on concentration histories of extracted caffeine at 13.8 MPa and mass-flow rate 1.51 g/min.

Points represent experimental data; lines are predicted results.

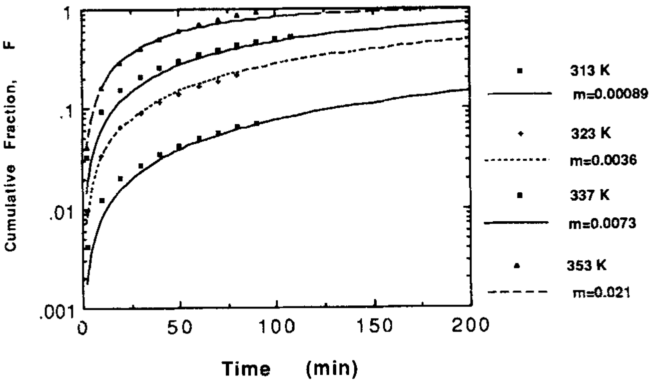

Figure 7. **Effect of temperature on cumulative fraction of caffeine extracted vs. time at 13.8 MPa and mass-flow rate 1.51 g/min.**

Points represent experimental data; lines are predicted results.

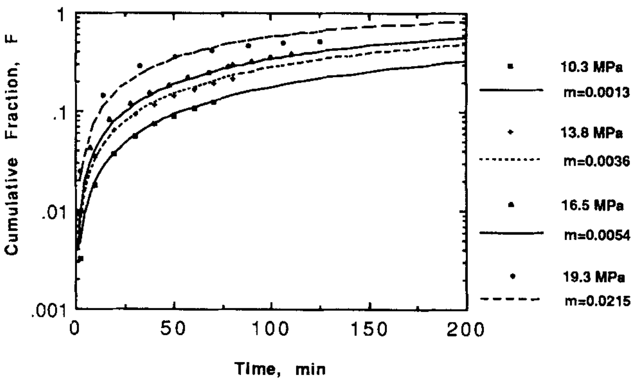

Figure 9. **Effect of pressure on cumulative fraction of caffeine extracted vs. time at 323 K and mass-flow rate 1.51 g/min.**

Points represent experimental data; lines are predicted results.

m that successfully described the experimental data except for the highest values of temperature and pressure. This is shown by the agreement of lines and data in Figures 6-9. At the highest values of temperature and pressure, the data are quite sensitive to fluctuations in operating conditions. Measured concentrations at these conditions (353 K and 19.3 MPa) had poor reproducibility, and could not be fitted well with the model (Figures 6 and 8). The cumulative fraction data (Figures 7 and 9), however, were in good agreement with the model for values of *m* determined from Figures 6 and 8, respectively. This supports the earlier statement that cumulative-fraction data are less sensitive to process parameters than concentration history data and less useful for discriminating between models.

Figures 10 and 11 (Tables 3 and 4) show values of the partition coefficient determined from the analysis of the data. The partition coefficient increases exponentially with both T and P. McHugh and Krukonis (1986) reported values of $m' = 0.03$-0.04 (wt. basis) at 4,500 psi (306 atm or 31.1 MPa) and 353 K. Paulaitis et al. (1983) reported values of $m' = 0.154$ and 0.174 (wt. basis) for neat caffeine in water (50 MPa, 292 K) and $m' = 0.054$ for coffee (45 MPa, 291 K). These values in Figure 11 are consistent with our values (converted to weight basis). The increase of the partition coefficient with pressure is evident. Ghonashi et al. (1991) recently reported values of partition coefficients for four organics distributed between supercritical CO_2 and water. Experimental and computed values generally increased with pressure, but demonstrated a crossover behavior with respect to temperature, increasing with temperature only at higher pressures. Their values, even for the most polar system, phenol distributed between CO_2 and water, were higher than our values and those reported in the literature.

Conclusion

The objective of this work has been to provide experimental data and a method of analysis for the dynamic process of supercritical extraction from porous material. The particular system studied, the decaffeination of coffee beans, has several

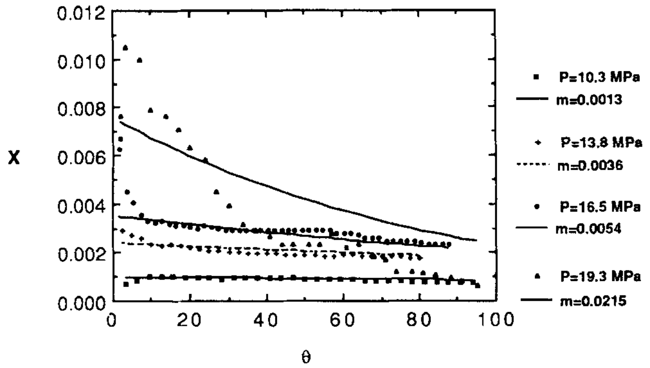

Figure 8. **Effect of pressure on concentration histories of extracted caffeine at 323 K and mass-flow rate 1.51 g/min.**

Points represent experimental data; lines are predicted results.

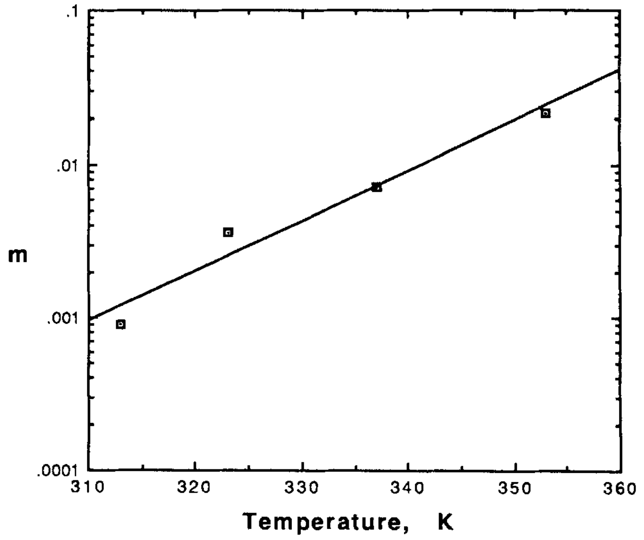

Figure 10. **Partition coefficient *m* (concentration basis) of caffeine for water-soaked coffee beans at 13.8 MPa and four different temperatures.**

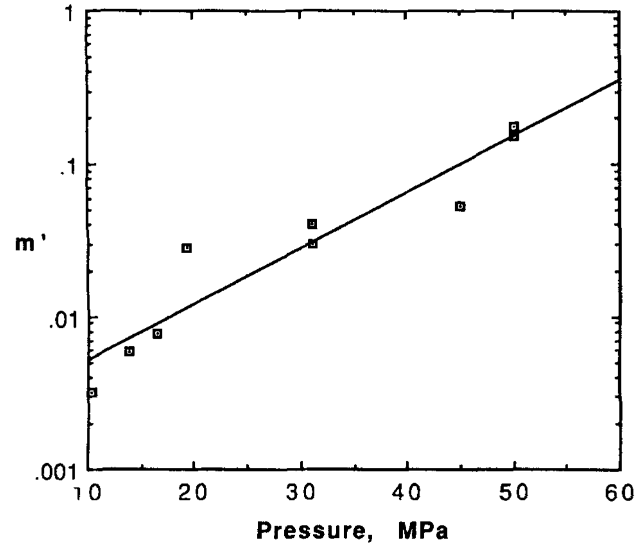

Figure 11. Partition coefficient m' (weight basis) of caffeine.

interesting features, some of which are of general applicability and some quite specific to decaffeination. Although extraction with supercritical CO_2 is believed to be highly selective for caffeine, the total extracted organic compound determined by our procedure may be larger than the content of caffeine found by specific quantitative analyses. Experience with large-scale commercial facilities, however, demonstrates that flavor components, released only during roasting, are not extracted during the decaffeination. Saturating the raw beans with water and humidifying the supercritical CO_2 are essential if high extraction rates are to be realized. Extraction rates increase at higher temperatures and pressures, due to the increased value of the partition coefficient for caffeine between supercritical CO_2 and water. Dynamic extraction data, that is, caffeine concentration histories, determined by monitoring the effluent of a continuous flow of supercritical CO_2 through a differential bed of coffee beans, can be described by a simple mathematical model. The model includes the effects of intraparticle diffusion, external film mass transfer, and partitioning of the caffeine between the water in the water-saturated beans and the flowing supercritical CO_2. This partition coefficient is the only free parameter in the proposed model for analyzing the extraction rate data.

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Notation

a_o, b_o, c_o = dimensions of the ellipsoidal coffee bean, cm
a_1, a_2 = eigenvalues defined in Eqs. 16 and 17
a_p = ratio of spherical coffee bean area per volume, 1/cm
$A = -B$ = quantities defined by Eqs. 15 and 18
b_1, b_2 = parameters in the parabolic concentration profile, defined in Eq. A4
b, c = parameters defined in Eqs. 19 and 20
Bi = Biot number, $(k_f R/D_e)$
c = caffeine concentration in CO_2 in the bed void volume, g/mL
c_i = caffeine concentration in the pore volume of the coffee bean, g/mL of pore volume
c_{io} = initial caffeine concentration in the pore volume of the coffee bean, g/mL pore volume
$\langle c_i \rangle$ = average caffeine concentration in the pore volume of the coffee bean, g/mL
c_s = sorbed caffeine concentration in the coffee bean, g/mL volume of solid fraction of beans
c_o = total caffeine concentration in the coffee bean, g/mL of wet bean volume
D = binary diffusion coefficient for caffeine in water, cm^2/s
D_{ab} = binary diffusion coefficient for caffeine in supercritical CO_2, cm^2/s
D_e = effective intraparticle diffusion coefficient for caffeine in the coffee bean, cm^2/s
F = cumulative fraction of caffeine extracted
k_a = adsorption rate constant, 1/s
k_f = external mass-transfer coefficient, cm/s
k_p = combined mass-transfer coefficient $(k_p' a_p)$, 1/s
k_p' = combined mass-transfer coefficient (k_p/a_p), cm/s
K = equilibrium adsorption coefficient, defined by Eq. 4
m = partition coefficient of caffeine distributed between supercritical CO_2 and water: conc. of caffeine in CO_2/conc. of caffeine in water
m' = partition coefficient (wt. basis): ratio of [wt. caffeine/wt. CO_2] to [wt. caffeine/wt. water]
M = mass of caffeine, g
N = proportionality constant for calibration of FID, g/cm^2
P = pressure, MPa
P_r = reduced pressure, P/P_c
Q = volumetric flow rate of supercritical CO_2, cm^3/s
r = radial position in spherical coffee bean, cm
R = radius of coffee bean, cm
Re = Reynolds number, $(2Ru\rho/\mu)$
t = time, s
T = temperature, K
T_r = reduced temperature, T/T_c
S = source or sink term, defined in Eq. A1
Sc = Schmidt number, $(\mu/\rho D_{ab})$
u = superficial velocity in bed, cm/s
V = volume of coffee bean, cm^3
x = dimensionless caffeine concentration in effluent (c/c_o)
y = dimensionless caffeine concentration in pores (c_i/c_o)
z = measured signal from FID

Greek letters

α = void fraction in bed
β = porosity of wet bean
ϕ = dimensionless mass-transfer coefficient $(k_p \tau)$, defined in Eq. 10
θ = dimensionless time (t/τ)
ρ = density of the coffee bean, g/cm^3
ρ_{solid} = density of the solid part of coffee bean, g/cm^3
τ = total bed volume/volumetric flow rate, s

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Appendix: Linear Driving-Force Mass-Transfer Coefficient

The differential mass-balance equation for $c_i(r, t)$, the concentration of caffeine in the water-soaked coffee bean is:

$$\beta \frac{\partial c_i}{\partial t} = D_e \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_i}{\partial r} \right) + S \qquad \text{(A1)}$$

in terms of a general source or sink term, S, which represents the adsorption-desorption rate process. The boundary conditions are:

$$\partial c_i/\partial r = 0 \qquad \text{at } r = 0 \qquad \text{(A2)}$$

and

$$D_e \partial c_i/\partial r = k_f[c - mc_i(R)] \qquad \text{at } r = R \qquad \text{(A3)}$$

in terms of k_f, the external mass-transfer coefficient, and $a_p = 3/R$. In writing Eq. A3 we recognize that the surface concentration of the water-soaked coffee bean, $c_i(R)$, is in equilibrium with the supercritical CO_2 at the surface; hence, c at the surface is $mc_i(R)$.

The linear driving-force model is based on the parabolic profile approximation to the intraparticle concentration profile:

$$c_i(r, t) = b_1(t) + b_2(t) r^2 \qquad \text{(A4)}$$

which is known to be a good approximation, except for small values of time (Do and Rice, 1986). The volume average of the concentration in the spherical particle, written simply as $c_i(t)$ in the main text, is defined by:

$$\langle c_i \rangle = (3/4\pi R^3) \int_o^R c_i(r) 4\pi r^2 dr \qquad \text{(A5)}$$

which from Eq. A4 gives:

$$\langle c_i \rangle = b_1 + (3/5) b_2 R^2 \qquad \text{(A6)}$$

Substituting $c_i(R)$ and $\partial c_i/\partial r$ from Eq. A4 into the boundary condition Eq. A3 yields a result that can be solved for c:

$$c = mb_1 + b_2 R^2 (m + 2/Bi) \qquad \text{(A7)}$$

Combining Eqs. A7 and A6 gives an expression for the concentration difference, $c - m\langle c_i \rangle$, that can be used to solve for b_2:

$$b_2 = [c - m\langle c_i \rangle]/R^2(2/Bi + m2/5) \qquad \text{(A8)}$$

Next, we volume-average Eq. A1 to get:

$$\beta \partial \langle c_i \rangle/\partial t = 6 b_2 D_e + \langle S \rangle \qquad \text{(A9)}$$

which, when combined with Eq. A8 to eliminate b_2, yields the differential mass-balance equation with the linear driving-force expression:

$$\beta \partial \langle c_i \rangle/\partial t = k_p[c - m\langle c_i \rangle] + \langle S \rangle \qquad \text{(A10)}$$

where

$$k_p = (15 k_f/R)/(5 + mBi) \qquad \text{(A11)}$$

When $m = 1$, Eqs. A10 and A11 reduce to the expressions of Do and Rice (1986) for the linear driving-force approximation.

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