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Mass Transfer Model for Supercritical Fluid Extraction Tests

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ABSTRACT

A mass transfer model using a linear equilibrium isotherm is presented for the static and dynamic stages of supercritical fluid extraction tests. In the static stage the fraction extracted is a function of a dimensionless time and a dimensionless equilibrium parameter. In the dynamic stage the fraction recovered is a function of a different dimensionless time, the same equilibrium parameter, and a dimensionless mass transfer parameter. Fitting the model to experimental extraction curves showed that increasing the pressure or density increases the equilibrium constant and decreases the overall mass transfer coefficient.

INTRODUCTION

Sample analysis by supercritical fluid extraction (SFE) is increasingly used due to its simplicity, high efficiency, and ease of analyte recovery. The SFE test is rapid; extraction time can be in the order of minutes, while in conventional liquid extraction it may require hours to achieve full recovery of the components. These results are consequences of the rapid transport rates and the increased solubilities in a supercritical fluid at high pressure (being similar to a liquid).

The SFE test usually consists of three steps. First, the extraction vessel containing the sample is filled with supercritical fluid and pressurized. Second, the sample contacts the supercritical fluid (SF) for a period of time, called the

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static stage. During this stage, much of the analyte transfers into the supercritical phase. Third, the extraction vessel is swept (or the SF phase is displaced) by fresh SF during a dynamic stage. The displaced SF, carrying the analyte, flows at atmospheric pressure to a collection vessel filled with an organic solvent such as acetone where, upon depressurization, the SF is converted into gas and the analyte is released into the organic solvent.

SFE is used to recover analytes from liquid or solid samples for subsequent analysis (1–4) or to extract solutes (5–7). In analytical usage the extraction vessels are small (1–4), but long beds may be used in extraction (5–8). If the material to be extracted, e.g., a metal, is only slightly soluble in the SF, a chelating agent may be added.

In the analytical literature no physical models for SFE have been proposed although Wang and Marshall (4) noted that the dynamic behavior of the test could be described as a biphasic exponential decay. Mass transfer models for SFE have been proposed by several workers (5–8) for extraction of components from packed beds of soil. In these models, flow and axial dispersion are important. In this paper a simple model is developed for SFE tests in the small extraction vessels used in analytical work.

MASS TRANSFER MODEL

The model is based on solute mass balances for the supercritical phase and the sample phase in the static and dynamic stages. Mass transfer during the pressurizing step is neglected. The assumptions are: 1) the two phases in the extraction vessel and the liquid in the collection vessel are well-mixed; 2) the extraction rate is described by an overall mass transfer coefficient; 3) the solute concentration in the solid is uniform: 4) solute equilibrium is described by a linear isotherm.

For the supercritical fluid phase, the solute mass balance is

$$\varepsilon V \frac{dc}{dt} = -(1 - \varepsilon) V \rho_s \frac{dq}{dt} - Qc \tag{1}$$

where c is the concentration of solute in the bulk of SF phase, q is the mass fraction of solute in the bulk of the sample, ε is the volume fraction which is occupied by the SF phase, V is the total volume of the extraction vessel, ρ_s is the sample density (for porous particulate samples, ρ_s is the solid wall density), Q is the volumetric flow rate, and t is the time. Equation (1) is applicable to the two stages, with $Q = 0$ for the static stage.

The mass balance for the sample phase is

$$dq/dt = -K_c a(Kq - c) \tag{2}$$

where K_c is the overall mass transfer coefficient, a is the specific surface area of the sample, and K is the distribution coefficient. Subsequently, the concentrations in Eqs. (1) and (2) are nondimensionalized using q_0 for q and Kq_0 for c, where q_0 is the original extractable mass fraction of solute in the sample. The subscripts "s" and "d" denote static and dynamic stages, respectively.

Static Stage

In dimensionless forms, Eqs. (1) and (2) become

$$\frac{dc_s}{d\tau} = -\frac{1}{K_e}\frac{dq_s}{d\tau} \tag{3}$$

$$dq_s/d\tau = -K_e\,(q_s - c_s) \tag{4}$$

where K_e is the dimensionless equilibrium constant:

$$K_e = \left[\frac{\varepsilon}{(1-\varepsilon)}\right]\frac{K}{\rho_s} \tag{5}$$

τ is the dimensionless static time:

$$\tau = k_s t \tag{6}$$

and k_s is the volumetric mass transfer coefficient for the static stage multiplied by the volume ratio of the phases:

$$k_s = (K_c\rho_s a)_s\left[\frac{1-\varepsilon}{\varepsilon}\right] \tag{7}$$

The initial conditions are:

$$\text{at } \tau = 0, \qquad c_s = 0 \tag{8}$$

$$\text{at } \tau = 0, \qquad q_s = 1.0 \tag{9}$$

The solutions of Eqs. (3) and (4) are

$$c_s = \frac{1 - \exp[-(1 + K_e)\tau]}{(1 + K_e)} \tag{10}$$

$$q_s = \frac{1 + K_e\exp[-(1 + K_e)\tau]}{(1 + K_e)} \tag{11}$$

The fractional extraction during the static stage, Y_s, expressed as mass extracted into the SF phase divided by the total initial extractable mass in the sample, is given by

$$Y_s = K_e c_s \tag{12}$$

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For long contact times, equilibrium fractional extraction, Y_{se}, is approached, where

$$Y_{se} = \frac{K_e}{1 + K_e} \tag{13}$$

Dynamic Stage

For the dynamic stage:

$$\frac{dc_d}{d\theta} = -\frac{1}{K_e}\frac{dq_d}{d\theta} - c_d \tag{14}$$

$$dq_d/d\theta = -K_e k_d(q_d - c_d) \tag{15}$$

where k_d is a dimensionless volumetric mass transfer coefficient for the dynamic stage:

$$k_d = (K_c \rho_s a)_d \left(\frac{\varepsilon V}{Q}\right)\left[\frac{1-\varepsilon}{\varepsilon}\right] \tag{16}$$

and θ is the dimensionless time defined as follows:

$$\theta = t_d\left(\frac{Q}{\varepsilon V}\right) \tag{17}$$

where t_d is the time measured from the beginning of the dynamic stage. The initial conditions for the dynamic stage are the final conditions of the static stage:

$$\text{at} \quad \theta = 0, \qquad c_d = c_{sf} \tag{18}$$

$$\text{at} \quad \theta = 0, \qquad q_d = q_{sf} \tag{19}$$

where c_{sf} and q_{sf} are the values of c_s and q_s at the end of the static stage when $\tau = \tau_s$. The solutions of Eqs. (14) and (15) are

$$c_d = \frac{1}{s_1} e^{-s_3\theta}\{c_{sf}[(s_1 - s_2)e^{s_1\theta} + s_2] + k_d q_{sf}[e^{s_1\theta} - 1]\} \tag{20}$$

$$q_d = \frac{1}{s_1} e^{-s_3\theta}\{q_{sf}[(s_1 - s_2) + s_2 e^{s_1\theta}] + k_d K_e c_{sf}[e^{s_1\theta} - 1]\} \tag{21}$$

where s_1–s_3 are functions of K_e and k_d as follows:

$$s_1 = +\sqrt{1 + 2k_d(1 - K_e) + [k_d(1 + K_e)]^2} \tag{22}$$

$$s_2 = \frac{1}{2}[1 + k_d(1 - K_e) + s_1] \tag{23}$$

$$s_3 = \frac{1}{2}[1 + k_d(1 + K_e) + s_1] \tag{24}$$

Collection Vessel

The collected fraction of the analyte (y) is obtained by noting that the mass of analyte collected is the initial mass less the amount remaining in the extraction vessel:

$$y = 1 - q_d - K_e c_d \tag{25}$$

RESULTS AND DISCUSSION

Static Stage

In SFE tests the static stage is usually planned for the recovery of a major portion of the extractable component from the sample. Equations (10)–(12) indicate that c_s, q_s, and Y_s approach their equilibrium values closely for $\tau > 2/(1 + K_e)$. The model was fitted to the static stage data of Laintz et al. (3) for their isothermal experiments at different pressures (yielding different densities of SF). Figure 1 shows a comparison between the Y_s data and the model. The fitted parameters, K_e and k_s, are given in Table 1, which also includes the values of K_e estimated from the limiting case, Eq. (13), using the final Y_s point. The

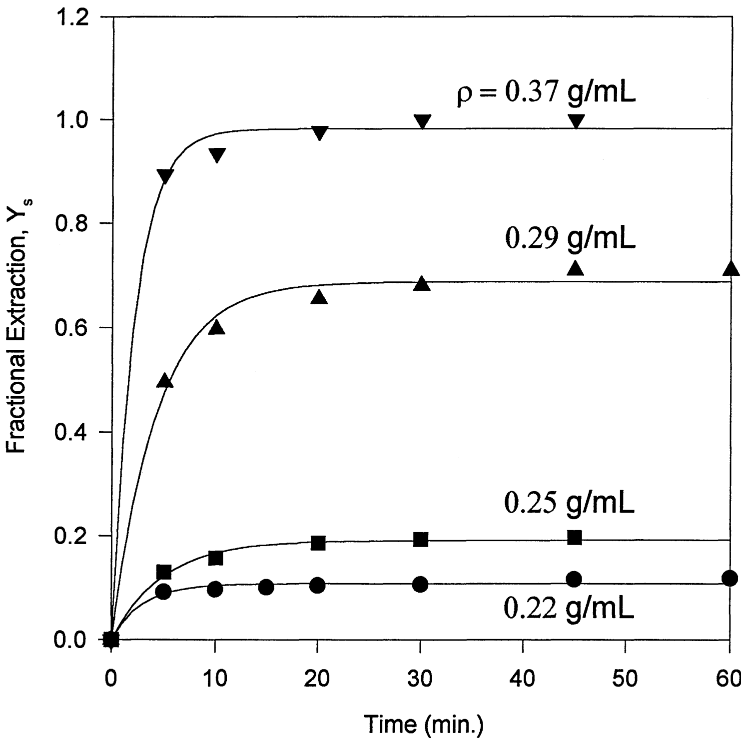

FIG. 1 Comparison between static SFE data of Laintz et al. (3) and model curves for the extraction of Cu^{2+} from stirred liquid samples with SF-CO_2 at different densities.

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TABLE 1
Fitted Parameters for the Static SFE Data of Laintz et al. (3), Shown in Fig. 1

	Parameters, Eqs. (10) & (12)		
SF density (g/mL)	k_s (min^{-1})	K_e	K_e from Eq. (13)
0.22	0.30	0.12	0.13
0.25	0.17	0.24	0.24
0.29	0.073	2.2	2.4
0.37	0.0082	56	>50

two values of K_e agree closely. The equilibrium constant, i.e., the solubility, increases with increasing SF density, as reported previously (9–11). The volumetric mass transfer coefficient decreases with density (or pressure) because the diffusion coefficient in the SF phase decreases with increasing pressure.

Dynamic Stage

During the dynamic stage, the mass fraction in the sample phase, q_d, decreases continuously as solute is released. The solution for q_d, Eq. (21), has two time constants, s_1 and s_3. At short times the dynamic behavior is characterized by s_3 while at large times by s_1, yielding a biphasic behavior in agreement with the empirical observations of Wang and Marshal (4). If the static stage is short, the concentration in the SF phase, c_d, may go through a maximum as shown in Fig. 2 where c_d is plotted against dimensionless dynamic time following static stages of different durations, τ_s. If τ_s is small, c_d increases initially; while for sufficiently large τ_s, c_d decreases continuously. This behavior is the result of two competing processes: solute is released from the sample and solute is washed out of the vessel by the SF. The c_d curve rises if the rate of release of solute from the sample exceeds the washout rate from the extraction vessel. The initial slope of the c_d curve is positive when

$$-\frac{1}{K_e}\frac{dq_d}{d\theta} > c_d \tag{26}$$

Combining Eqs. (10), (11), (15), (18), (19), and (26) shows that the c_d curve rises initially if

$$\tau_s < \frac{1}{1 + K_e}\ln[1 + k_d(1 + K_e)] \tag{27}$$

Figure 2 shows c_d curves for different values of τ_s with $K_e = 2$ and $k_d = 0.1$. For these values, Eq. (27) indicates that the c_d curve will go through a maxi-

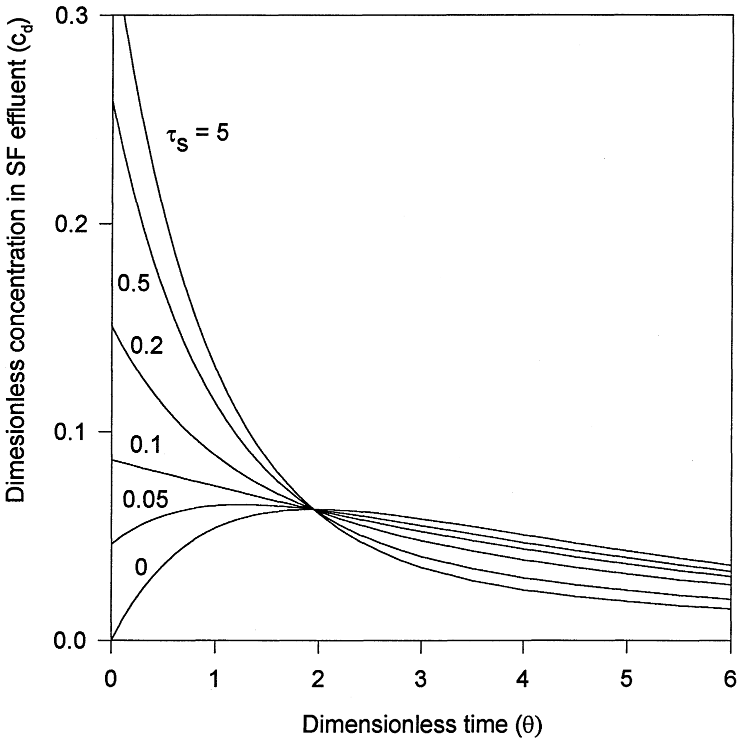

FIG. 2 Effect of the dimensionless static time on the c_d curve for $K_e = 2$ and $k_d = 0.1$.

mum if $\tau_s < 0.087$, in agreement with the curves shown in the figure. When there is a maximum in the c_d curve, there is an inflection point in the y curve.

The effect of the dimensionless equilibrium constant on the dynamic SFE curves is shown in Fig. 3 for $\tau_s = 0.5$ and $k_d = 0.1$. For the same dimensionless time, increasing the equilibrium constant by increasing the pressure increases the yield of extraction as observed experimentally by Thurbide et al. (1) and Al-Jabari and Thurbide (2). At a pressure of 200 atm their static time of 30 minutes resulted in almost full recovery of the metal component, and the subsequent dynamic stage behaved essentially as a CSTR. With decreasing pressure their measured dynamic extraction curves were shifted from the CSTR curve to longer times, similar to the curves in Fig. 3.

The model was fitted to the SFE data of Al-Jabari and Thurbide (2) at different pressures by assuming that the amount of analyte collected at the longest time at the highest pressure (200 atm) represented complete recovery of the extractable metal. Figure 4 shows the comparison between the experimental and the theoretical dynamic SFE curves. With the parameters given in Table 2, the model gave a good fit to the data. As for static SFE tests (Table 1), the equilibrium constant increases with increasing pressure (or density) and the volumetric mass transfer coefficient decreases with pressure.

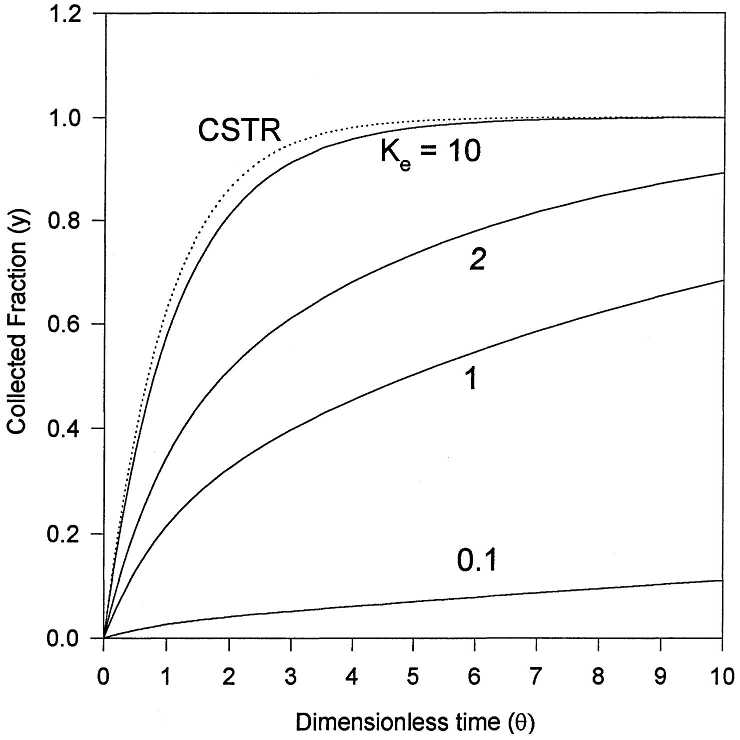

FIG. 3 Effect of the dimensionless equilibrium constant on the dynamic SFE curves for $k_d = 0.1$ and $\tau_s = 0.5$.

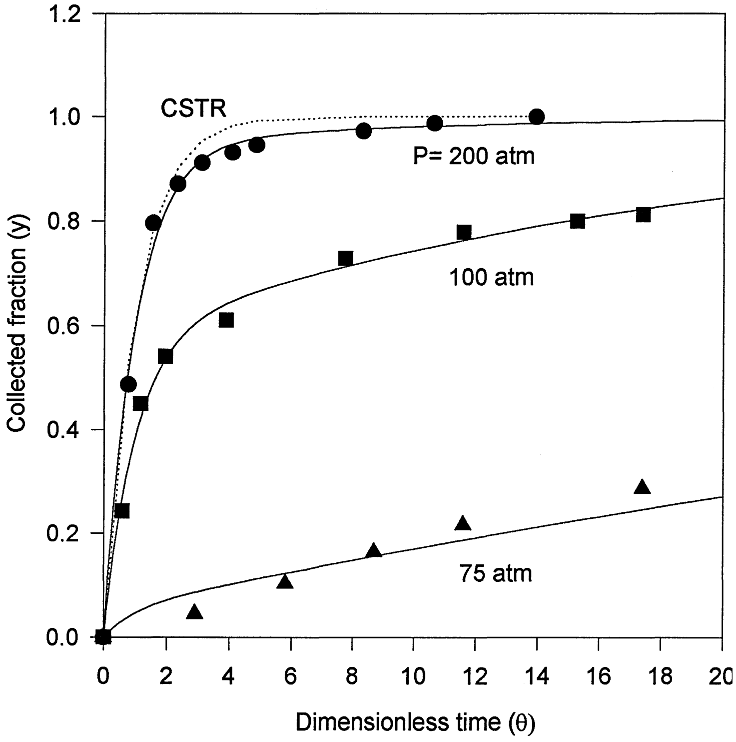

FIG. 4 Comparison between dynamic SFE data of Al-Jabari and Thurbide (2) and model curves for the extraction of Mn from pulp fibers with SF-CO_2 at different pressures.

TABLE 2
Fitted Parameters for the Dynamic SFE Data of Al-Jabari and Thurbide (2), Shown in Fig. 4

Pressure (atm)	K_e	$k_d \times 10^3$	τ_s
75.0	1.7	7.9	0.042
100	7.5	6.7	0.14
200	21	5.1	Large

CONCLUSIONS

The simple two-parameter mass transfer model provided a good fit to experimental SFE curves for the extraction of metal ions from solid and liquid samples for static extraction as well as two-stage extraction. Increasing the pressure (or density) of the supercritical phase increased the equilibrium constant and decreased the mass transfer coefficient in accord with expectations. SFE tests can be completed more rapidly by increasing the equilibrium constant, the mass transfer coefficient, as well as the length of the static stage. When these parameters are sufficiently large, the dynamics of the process approach that of a CSTR. Such conditions can be achieved at high pressure and high flow rate and with a moderate static time.

NOMENCLATURE

a	specific surface area of the sample ($\mathrm{cm}^2 \cdot \mathrm{g}^{-1}$)
c	concentration of the solute in the bulk of SF phase ($\mathrm{g} \cdot \mathrm{cm}^{-3}$)
c_d	dimensionless concentration of the solute in the bulk SF phase during the dynamic stage
c_s	dimensionless concentration of the solute in the bulk SF phase during the static stage
c_{sf}	dimensionless concentration of the solute in the bulk SF phase at the end of the static stage
K	distribution coefficient ($\mathrm{cm}^3 \cdot \mathrm{g}^{-1}$)
K_e	dimensionless equilibrium constant
K_c	overall mass transfer coefficient ($\mathrm{cm} \cdot \mathrm{s}^{-1}$)
k_d	volumetric mass transfer coefficient for the dynamic stage defined in Eq. (16)
k_s	volumetric mass transfer coefficient for the static stage defined in Eq. (7) (s^{-1})
q	mass fraction of the solute in the bulk of the sample
Q	volumetric flow rate ($\mathrm{cm}^3 \cdot \mathrm{s}^{-1}$)
q_d	dimensionless mass fraction of the solute in the bulk of the sample during the dynamic stage

q_s	dimensionless mass fraction of the solute in the bulk of the sample during the static stage
q_{sf}	dimensionless mass fraction of the solute in the bulk of the sample at the end of the static stage
s_1	function defined in Eq. (22)
s_2	function defined in Eq. (23)
s_3	function defined in Eq. (24)
t	time (s)
t_d	time measured from the beginning of the dynamic stage (s)
V	total volume of the extraction vessel (cm^3)
y	fraction of the analyte collected during the dynamic stage
Y_s	fractional extraction during the static stage
Y_{se}	equilibrium fractional extraction during the static stage

Greek Letters

ε	volume fraction which is occupied by the SF phase
ρ	density of the SF (g·cm^{-3})
ρ_s	density of the sample (g·cm^{-3})
τ	dimensionless time during the static stage
τ_s	dimensionless time at the end of the static stage
θ	dimensionless time during the dynamic stage

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