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EQUILIBRIUM THEORY OF EXSORPTION: A GAS–LIQUID–ADSORBENT MASS-TRANSFER OPERATION

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Abstract—A three-phase (gas–liquid–adsorbent) mass-transfer operation, called *exsorption*, which may have potential in chemical, biochemical and environmental processes, is described. The system of interest consists of a column packed with adsorbent particles through which gas and liquid streams flow in countercurrent mode. Distributed-parameter models, which assume isothermal operation and transfer of a single solute among the mutually immiscible phases, are presented for the two different wetting states of adsorbent particles. Equilibrium theory of exsorption is established on the basis of the distributed-parameter models of the system. The equilibrium theory predicts various aspects of propagation dynamics of concentration waves and reveals individual–relative effects of concentration dependence of gas–liquid, liquid–adsorbent and gas–adsorbent equilibrium isotherms. Based on the characteristics of the equilibrium isotherms, criteria for the development of sharpening, spreading, and stagnant concentration waves can be obtained directly from the equilibrium propagation velocity of the system. The equilibrium theory of exsorption is compared with the equilibrium theories of fixed-bed adsorption and countercurrent gas–liquid mass-transfer operations.

INTRODUCTION

Many chemical processes taking place in continuous systems have mathematically similar distributed-parameter models and exhibit parallel dynamic behavior. Dynamic behavior of many processes (e.g. adsorption, absorption, distillation, extraction, sedimentation, filtration, freeze drying, crystallization, heat-exchanger dynamics) can be portrayed in terms of traveling mass and/or thermal waves (Marquardt, 1990). Propagation dynamics of mass/thermal waves can be investigated through numerical solution of rigorous or simplified distributed-parameter models. However, the results may be so obscured by the complex interdependence of the variables/parameters that it remains still a very difficult task to deduce underlying phenomena and to arrive at a theory. Therefore, it is desirable to obtain analytical solutions in order to capture explicit interdependence of principal variables/parameters and their direct effects on propagation dynamics of mass/thermal waves. Not all analytical solutions, however, provide functional closed-form expressions which display relationships among variables to the extent that their effect on wave-propagation phenomena can be observed explicitly. In such cases, critical phenomena of wave propagation may be predicted, at least qualitatively, through equilibrium approximation (i.e. contacting phases are assumed to be at local equilibrium in the limiting case as mass/heat-transfer coefficients approach infinity). Even though all processes have finite transfer coefficients, equilibrium theories of processes with distributed parameters establish a strong basis of wave-propagation dynamics. Although equilibrium theories cannot predict the behavior strictly at the system boundaries (Friedly, 1972; Rhee *et al.*, 1986), equilibrium approximation has greatly helped to advance theories of many processes such as temperature-swing and/or pressure-swing fixed-bed adsorption, moving-bed adsorption, countercurrent extraction, and other transfer operations (Ruthven, 1984; Yang, 1987; Hwang, 1987; Hwang and Helfferich, 1988, 1989; Marquardt, 1990).

In this work, a three-phase (gas–liquid–adsorbent) continuous countercurrent mass-transfer operation, called *exsorption*, is described and its distributed-parameter model is presented. Equilibrium theory of exsorption is derived on the basis of its distributed-parameter model. Wave-propagation dynamics of the system is investigated on the basis of its equilibrium theory. Effects of the gas–liquid, liquid–adsorbent and gas–adsorbent equilibrium isotherms on propagation dynamics of mass fronts are investigated. Criteria for development of sharpening, spreading, and stagnant concentration waves are obtained explicitly from the equilibrium propagation velocity of the system. It is demonstrated that, equilibrium theory of exsorption can draw on a strong basis of wave-propagation dynamics to assist in elucidating the confounding effects of phase and sorption equilibria on the dynamics of exsorption.

MODELING OF EXSORPTION

The word *exsorption* was used first by Kuo (Kuo, 1984), who introduced the idea of simultaneous solvent *extraction* and *adsorption*. Kuo showed that solute-removal capacity of this new process could be

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greater than those of extraction and adsorption processes, depending upon characteristics of the phase-equilibrium and sorption-equilibrium isotherms. Kuo conceived a simple isothermal batch operation for separation of multiple solute and based his conclusions exclusively on equilibrium effects. A distributed-parameter model for continuous countercurrent isothermal operation of exsorption was proposed by Shojaie (1987). Shojaie also gave consideration to possible contacting schemes of the gas and liquid phases with the adsorbent phase. Sunol *et al.* (1988) introduced *supercritical exsorption* (SCEXS) and presented experimental results obtained using aqueous phenol solution as the process stream, supercritical carbon dioxide as the solvent and activated carbon as the adsorbent. They also presented the numerical solution of a model of supercritical exsorption column, model parameters regressed from the experimental results, experimental and theoretical comparison of adsorption, supercritical extraction and supercritical exsorption processes. Akman *et al.* investigated operational policies (Akman *et al.*, 1988; Akman and Sunol, 1990) and environmental applications (Akman *et al.*, 1989) of supercritical exsorption. Detailed thermodynamics and distributed-parameter modeling along with some analytical solutions for various limiting-case conditions of supercritical exsorption can be found elsewhere (Akman and Sunol, 1991b; Akman, 1991c).

A simple prototype of a continuous countercurrent exsorption process is depicted in Fig. 1. The system consists of a fixed-bed packed with adsorbent particles over which solvent and process streams are in continuous contact. The process serves the purpose of recovering the solute(s) from the process stream (separation or purification). For single- or multi-solute systems, the advantages of countercurrent exsorption over adsorption and/or extraction processes are the prolonged bed activity and/or enhanced selectivity (depending on prevailing wetting conditions within the column, concentration dependence of gas–liquid partition coefficient, and individual–relative concentration dependence of the phase- and sorption-equilibrium isotherms) (Akman, 1991c). These advantages of countercurrent exsorption are greatly enhanced when the operation is conducted at supercritical-fluid conditions, and if the operating policies are selected to capitalize on the parametric sensitivity of supercritical-fluid solvent, the retrograde temperature effects on supercritical-phase sorption equilibria, and the solubility-sorption relationships at supercritical-fluid conditions (Akman, 1991c; Akman and Sunol, 1991a).

The performance and dynamics of an exsorption process depend on distribution of the phases involved, i.e. the wetting states that may prevail within the column. In conventional continuous separation operations such as extraction or absorption, the impact of wetting condition is largely on the gas–liquid interfacial area, and packing materials serve merely the purpose of increasing the interfacial area for mass transfer. In exsorption, however, adsorbent particles participate in the mass-transfer mechanism and also affect the gas-liquid interfacial area. Therefore, the effect of wetting states is more complex and important in exsorption than conventional continuous gas–liquid mass-transfer operations. The three cases of wetting states that may prevail within an exsorption column are (pictorially shown in Fig. 2):

Case I (*complete wetting*): adsorbent particles are completely wetted by the liquid phase (which is the most probable case that may prevail in subcritical-region operation of exsorption, i.e. with a low-density gas solvent). There is no gas–solid contact. Gas–liquid mass transfer and adsorption from the liquid phase occur simultaneously.

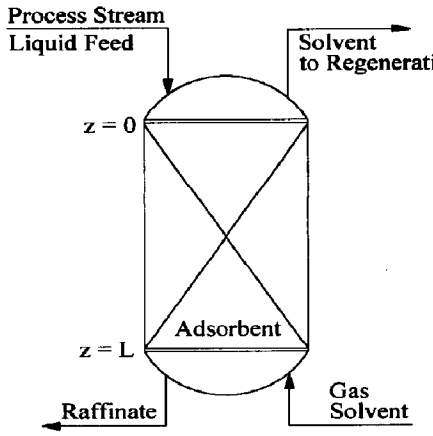


Fig. 1. The exsorption column.

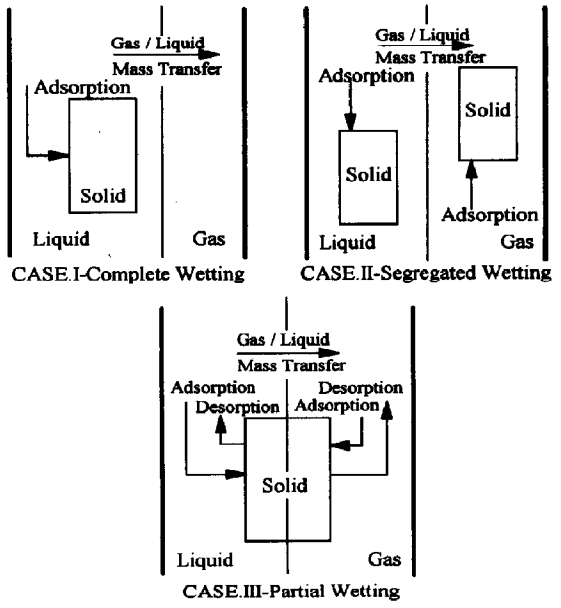


Fig. 2. Possible wetting states of adsorbent particles.

Case II (*segregated wetting*): the gas and liquid phases flow countercurrently in segregated-flow pattern (which is the probable case that may prevail in supercritical-region operation of exsorption, i.e. with a dense-gas solvent). The adsorbent particles that lie in the region occupied by the liquid phase are in contact only with the liquid phase, and the adsorbent particles that lie in the region occupied by the gas phase are in contact only with the gas phase. Gas–liquid mass transfer, adsorption from the liquid phase, and adsorption from the gas phase occur simultaneously.

Case III (*partial wetting*): adsorbent particles are partially and randomly wetted by the liquid and gas phases. There exist both liquid–solid and gas–solid contact. Gas–liquid mass transfer, adsorption from the liquid–gas phases, and desorption into the gas–liquid phase occur simultaneously (depending on solute concentration in the gas and liquid phases, and the solute-loading level of the adsorbent).

The partial-differential-equation models for cases I and II wetting conditions of exsorption are given in Tables 1 and 2. Case III wetting condition of exsorption is outside the scope of this work since it is not possible to derive a closed-form expression for equilibrium theory of exsorption for the partial/random wetting case (Akman, 1991c). The models assume that the gas and liquid phases are immiscible and the solute is the only adsorbed component. Glueckauf-type linear-rate expressions (Ruthven, 1984; Yang, 1987) are used to describe solute uptake of the adsorbent phase.

EQUILIBRIUM THEORY OF EXSORPTION

In this section, equilibrium theory of exsorption is derived for plug-flow, segregated-wetting system (case II). As will be shown, equilibrium theory of exsorption for the complete-wetting condition (case I) can be obtained directly from the segregated-wetting model.

For each of the wetting cases, dynamics of an exsorption column depends on the nature (concentration dependence) of both the phase-equilibrium (gas–liquid) and the sorption-equilibrium (liquid–solid or gas–solid) isotherms. Therefore, equilibrium theory will be developed in two steps; first through *local sorption-equilibrium*, and then, through *local phase-equilibrium* approximations.

Local sorption-equilibrium approximation

The plug-flow version of the partial differential equations describing the solute movement in the liquid and gas phases for the segregated-wetting

Table 1. Model of the exsorption column for case I wetting conditions

Solute balance for the liquid phase:

$$\frac{\partial C_L}{\partial t} = + E_{zL}\frac{\partial^2 C_L}{\partial z^2} - \left(\frac{u_L}{\varepsilon_L}\right)\frac{\partial C_L}{\partial z} - \frac{K_{OG}a_G}{\varepsilon_L \rho_L}(C_G^* - C_G) - \left(\frac{1-\varepsilon}{\varepsilon_L}\right)\left(\frac{\rho_q}{\rho_L}\right)\frac{\partial q_L}{\partial t}$$

Solute balance for the gas phase:

$$\frac{\partial C_G}{\partial t} = + E_{zG}\frac{\partial^2 C_G}{\partial z^2} + \left(\frac{u_G}{\varepsilon_G}\right)\frac{\partial C_G}{\partial z} + \frac{K_{CG}a_G}{\varepsilon_G \rho_G}(C_G^* - C_G)$$

Solute balance for the adsorbent phase:

$$\frac{\partial q_L}{\partial t} = K_{sL}^p a_s (q_L^* - q_L)$$

Table 2. Model of the exsorption column for case II wetting conditions

Solute balance for the liquid phase:

$$\frac{\partial C_L}{\partial t} = + E_{zL}\frac{\partial^2 C_L}{\partial z^2} - \left(\frac{u_L}{\varepsilon_L}\right)\frac{\partial C_L}{\partial z} - \frac{K_{OG}a_G}{\varepsilon_L \rho_L}(C_G^* - C_G) - \left(\frac{1-\varepsilon}{\varepsilon_L}\right)\left(\frac{\rho_q}{\rho_L}\right)\left(\frac{\varepsilon_L}{\varepsilon}\right)\frac{\partial q_L}{\partial t}$$

Solute balance for the gas phase:

$$\frac{\partial C_G}{\partial t} = + E_{zG}\frac{\partial^2 C_G}{\partial z^2} + \left(\frac{u_G}{\varepsilon_G}\right)\frac{\partial C_G}{\partial z} + \frac{K_{OG}a_G}{\varepsilon_G \rho_G}(C_G^* - C_G) - \left(\frac{1-\varepsilon}{\varepsilon_G}\right)\left(\frac{\rho_q}{\rho_G}\right)\left(\frac{\varepsilon_G}{\varepsilon}\right)\frac{\partial q_G}{\partial t}$$

Solute balance for the adsorbent phase in contact with the liquid:

$$\frac{\partial q_L}{\partial t} = K_{sL}^p a_s (q_L^* - q_L)$$

Solute balance for the adsorbent phase in contact with the gas:

$$\frac{\partial q_G}{\partial t} = K_{sG}^p a_s (q_G^* - q_G)$$

model of exsorption can be written as

$$\frac{\partial C_L}{\partial t} = -\left(\frac{u_L}{\varepsilon_L}\right)\frac{\partial C_L}{\partial z} - \frac{K_{OG}a_G}{\varepsilon_L\rho_L}(C_G^* - C_G) - \left(\frac{1-\varepsilon}{\varepsilon_L}\right)\left(\frac{\rho_q}{\rho_L}\right)\left(\frac{\varepsilon_L}{\varepsilon}\right)\frac{\partial q_L}{\partial t} \quad (1)$$

$$\frac{\partial C_G}{\partial t} = +\left(\frac{u_G}{\varepsilon_G}\right)\frac{\partial C_G}{\partial z} - \frac{K_{OG}a_G}{\varepsilon_G\rho_G}(C_G^* - C_G) - \left(\frac{1-\varepsilon}{\varepsilon_G}\right)\left(\frac{\rho_q}{\rho_G}\right)\left(\frac{\varepsilon_G}{\varepsilon}\right)\frac{\partial q_G}{\partial t}. \quad (2)$$

Assuming that the solid and fluid (liquid or gas) phases are at local equilibrium, the adsorbent loadings from the liquid and gas phases can be related to the liquid- and gas-phase mole fractions of the solute through their respective sorption-isotherm relationships as

$$q_L \approx q_L^*(C_L), \qquad \frac{\partial q_L}{\partial t} \approx \frac{\partial q_L^*}{\partial t} = \frac{dq_L^*}{dC_L}\left(\frac{\partial C_L}{\partial t}\right) \quad (3)$$

$$q_G \approx q_G^*(C_G), \qquad \frac{\partial q_G}{\partial t} \approx \frac{\partial q_G^*}{\partial t} = \frac{dq_G^*}{dC_G}\left(\frac{\partial C_G}{\partial t}\right). \quad (4)$$

Substitution of eqs (3) and (4) into eqs (1) and (2), respectively, leads to the following set of partial differential equations which describe the exsorption column dynamics under local solid–fluid equilibrium conditions:

$$\frac{\partial C_L}{\partial t} = -\omega_L(C_L)\frac{\partial C_L}{\partial z} - \frac{1}{\theta_L(C_L)}\frac{K_{OG}a_G}{h_L}[C_G^*(C_L) - C_G] \quad (5)$$

$$\frac{\partial C_G}{\partial t} = +\omega_G(C_G)\frac{\partial C_G}{\partial z} + \frac{1}{\theta_G(C_G)}\frac{K_{OG}a_G}{h_G}[C_G^*(C_L) - C_G] \quad (6)$$

where

$$\omega_L(C_L) = \frac{1}{\theta_L(C_L)}\left(\frac{u_L}{\varepsilon_L}\right) \quad (7)$$

$$\omega_G(C_G) = \frac{1}{\theta_G(C_G)}\left(\frac{u_G}{\varepsilon_G}\right). \quad (8)$$

$$\theta_L(C_L) = \left[1 + \left(\frac{1-\varepsilon}{\varepsilon_L}\right)\left(\frac{\rho_q}{\rho_L}\right)\left(\frac{\varepsilon_L}{\varepsilon}\right)\frac{dq_L^*}{dC_L}\right] \quad (9)$$

$$\theta_G(C_G) = \left[1 + \left(\frac{1-\varepsilon}{\varepsilon_G}\right)\left(\frac{\rho_q}{\rho_G}\right)\left(\frac{\varepsilon_G}{\varepsilon}\right)\frac{dq_G^*}{dC_G}\right] \quad (10)$$

$$h_L = \varepsilon_L\rho_L, \qquad h_G = \varepsilon_G\rho_G. \quad (11)$$

For an exsorption column operating under complete-wetting conditions, the above equations are still valid with the following modifications:

$$\theta_L(C_L) = \left[1 + \left(\frac{1-\varepsilon}{\varepsilon_L}\right)\left(\frac{\rho_q}{\rho_L}\right)\frac{dq_L^*}{dC_L}\right], \quad \theta_G = 1. \quad (12)$$

In the above equations, ω_L and ω_G are the propagation velocities of mass fronts in the liquid and gas phases, respectively. These propagation velocities are composition dependent if the derivatives of the sorption-isotherm relationships [eqs (3) and (4)] with respect to the liquid- and gas-phase solute concentrations are not constant. Since, for any system, $\theta_L \geq 1$ and $\theta_G \geq 1$, the propagation velocities of the mass fronts are lower than the superficial velocities of the liquid and gas phases. Therefore, much longer breakthrough times are observed in exsorption compared to extraction. Also, for more favorable sorption isotherm(s)—for isotherm(s) with a higher degree of curvature but with identical maximum-loading capacity—(i.e. $d^2q_L/dC_L^2 < 0$ and $d^2q_G/dC_G^2 < 0$; e.g. for a Langmuir-type adsorption isotherm), magnitudes of the derivative terms in eqs (9) and (10) increase, and hence, the breakthrough time increases. Therefore, the sorption-equilibria-dependent dynamic behavior of an exsorption column can be explained–predicted based on local sorption-equilibrium approximation. Since, in many real systems, solid–fluid mass-transfer coefficients are much higher than gas–liquid mass-transfer coefficients, the equilibrium-sorption approximation should predict propagation dynamics of mass fronts in an exsorption column with reasonable accuracy. For a completely linear system (i.e. for linear phase equilibrium and linear sorption equilibria), with constant propagation velocities, an analytical solution to the set of partial differential equations [eqs (5) and (6)] can be obtained (Hwang, 1987).

Local phase-equilibrium approximation

The complete equilibrium theory of exsorption can be derived starting from the equilibrium-sorption model of exsorption [eqs (5) and (6)] which may be rewritten as

$$\theta_L(C_L)h_L\left\{\frac{\partial C_L}{\partial t} + \omega_L(C_L)\frac{\partial C_L}{\partial z}\right\} + K_{OG}a_G[C_G^*(C_L) - G_G] = 0 \quad (13)$$

$$\theta_G(C_G)h_G\left\{\frac{\partial C_G}{\partial t} - \omega_G(C_G)\frac{\partial C_G}{\partial z}\right\} - K_{OG}a_G[C_G^*(C_L) - C_G] = 0. \quad (14)$$

The overall material balance is the sum of eqs (13) and (14):

$$\theta_L(C_L)h_L\left\{\frac{\partial C_L}{\partial t} + \omega_L(C_L)\frac{\partial C_L}{\partial z}\right\} + \theta_G(C_G)h_G\left\{\frac{\partial C_G}{\partial t} - \omega_G(C_G)\frac{\partial C_G}{\partial z}\right\} = 0. \quad (15)$$

Assuming that the liquid and gas phases are at local equilibrium, the mole fraction of the solute in the gas phase and its partial derivatives can be related to the

liquid-phase mole fraction of the solute as

$$C_G \approx C_G^*(C_L), \quad \frac{\partial C_G}{\partial t} \approx \frac{\partial C_G^*}{\partial t} = \frac{dC_G^*}{dC_L}\left(\frac{\partial C_L}{\partial t}\right),$$
$$\frac{\partial C_G}{\partial z} \approx \frac{\partial C_G^*}{\partial z} = \frac{dC_G^*}{dC_L}\left(\frac{\partial C_L}{\partial z}\right). \tag{16}$$

Substitution of the above equalities into the overall material balance [eq. (15)] leads to the following hyperbolic partial differential equation in terms of the liquid-phase solute mole fraction:

$$\frac{\partial C_L}{\partial t} + \Phi(C_L)\frac{\partial C_L}{\partial z} = 0. \tag{17}$$

In this wave equation, the equilibrium propagation velocity of concentration waves depends on the phase- and sorption-equilibrium relationships as

$$\Phi(C_L) = \left\{ \frac{\left(\frac{u_L}{\varepsilon_L}\right) - \left(\frac{u_G}{\varepsilon_G}\right)\left(\frac{h_G}{h_L}\right)\frac{dC_G^*(C_L)}{dC_L}}{\theta_L(C_L)\left[1 + \left(\frac{\theta_G(C_L)h_G}{\theta_L(C_L)h_L}\right)\frac{dC_G^*(C_L)}{dC_L}\right]} \right\} \tag{18}$$

where

$$\theta_L(C_L) = \left[1 + \left(\frac{1-\varepsilon}{\varepsilon_L}\right)\left(\frac{\rho_q}{\rho_L}\right)\left(\frac{\varepsilon_L}{\varepsilon}\right)\frac{dq_L^*(C_L)}{dC_L}\right] \tag{19}$$

$$\theta_G(C_L) = \left[1 + \left(\frac{1-\varepsilon}{\varepsilon_G}\right)\left(\frac{\rho_q}{\rho_G}\right)\left(\frac{\varepsilon_G}{\varepsilon}\right)\frac{dq_G^*(C_G^*(C_L))}{dC_L}\right] \tag{20}$$

For an exsorption column operating under complete-wetting conditions, eqs (17), (18) and (12) are still valid.

Equation (17), which can also be written for the gas phase, represents a wave traveling with a unique velocity [equilibrium eigenvelocity, Hwang (1987)] in both the liquid and gas phases. The propagation velocity may be viewed (Hwang, 1987) as the ratio of the net convective transport of the mass-transfer capacity to the total capacity in all three phases (gas, liquid, and adsorbent phases).

For a completely linear system (linear phase equilibrium and linear sorption equilibria) the propagation velocity is constant (concentration independent), and hence, the wave travels as introduced, without any change in its shape. In this case, eq. (17) (advection equation) has the following simple analytical solution:

$$C_L(t, z) = \begin{cases} C_L^o, & z/\Phi \geq t \\ 0, & z/\Phi < t. \end{cases} \tag{21}$$

Equation (21) may be used in estimation of the breakthrough time of the solute in an exsorption column operating under the conditions of local linear phase-equilibrium and local linear sorption-equilibria.

Phase- and sorption-isotherm effects on wave-propagation behavior

The results [eqs (17)–(20)] obtained through local phase- and sorption-equilibrium approximations are valuable since the wave-propagation dynamics of countercurrent exsorption column can be predicted on the basis of the nature (concentration dependence) of the phase and sorption equilibria.

If the phase and/or sorption equilibria are nonlinear, the propagation velocity of a positive step disturbance (a step increase in the liquid-phase feed concentration over zero fluid-phase concentration profile and zero adsorbent–loading profile) introduced in the liquid phase varies with concentration, and thus varies with location within a concentration wave as given by eq. (18). To clarify the picture, both the liquid- and gas-phase sorption-equilibrium relationships may be assumed as linear so that the concentration dependence of the propagation velocity can be attributed solely to the nonlinearity in the gas–liquid phase-equilibrium relationship. If the phase equilibrium is also linear (dC_G^*/dC_L = constant), then the system is fully linear (Φ = constant), and any liquid-phase concentration disturbance propagates with constant velocity without any change in its shape. If the phase equilibrium is of favorable type ($d^2C_G^*/dC_L^2 < 0$; e.g. for a Langmuir-type relationship), the propagation velocity decreases with increasing axial position within a wave. This can be explained as follows (Ruthven, 1984; Hwang and Helfferich, 1988). For a positive step disturbance in the liquid phase, the concentration decreases with increasing axial position and increases with decreasing axial position within a wave. For a favorable phase equilibrium relationship, the term dC_G^*/dC_L in eq. (18) increases with increasing axial position (towards the downstream end of the wave), and decreases with decreasing axial position (towards the upstream end of the wave). This being the case, with increasing axial position within a wave, the numerator of eq. (18) decreases while the denominator increases, and hence, the propagation velocity decreases with increasing axial position within a wave with decreasing concentration. However, with decreasing axial position within a wave with increasing concentration, the numerator of eq. (18) increases while the denominator decreases, and hence, the propagation velocity increases. Therefore, under favorable-type phase-equilibrium relationship, the upstream end of the wave tends to travel faster than the downstream end, leading to sharpening-type wave-propagation behavior. On the other end, if the phase equilibrium is of unfavorable type ($d^2C_G^*/dC_L^2 > 0$), the propagation velocity increases with increasing axial position within a wave. Therefore, under unfavorable-type phase equilibrium relationship, the downstream end of the wave tends to travel faster than the upstream end, leading to spreading-type wave-propagation behavior.

As a second step, to clarify the picture, both the phase-equilibrium relationship and the gas-phase sorption isotherm may be assumed as linear, so that

the concentration dependence of the equilibrium propagation velocity can be attributed solely to the nonlinearity in the liquid-phase sorption isotherm. If the liquid-phase sorption isotherm is linear (dq_L^*/dC_L = constant), then the system is fully linear (Φ = constant), and any liquid-phase concentration disturbance propagates with constant velocity without any change in its shape. If the liquid-phase isotherm is of favorable type ($d^2q_L^*/dC_L^2 < 0$), the propagation velocity decreases with increasing axial position within a wave. Therefore, for a favorable-type liquid-phase sorption isotherm, the upstream end of the wave tends to travel faster than the downstream end, leading to sharpening-type wave-propagation behavior. On the other end, if the liquid-phase sorption isotherm is of unfavorable type ($d^2q_L^*/dC_L^2 > 0$), the propagation velocity increases with increasing axial position within a wave. Therefore, under unfavorable-type liquid-phase isotherm, the downstream end of the wave tends to travel faster than the upstream end, leading to spreading-type wave-propagation behavior.

A similar argument can be carried out (for case II) to identify the effects of the nature of the gas-phase sorption isotherm by considering the phase-equilibrium and the liquid-phase sorption-isotherm relationships as linear. However, as can be seen from eq. (20), under local gas–liquid equilibrium conditions, the effect of the gas–liquid phase equilibrium relationship is transformed through the gas-phase sorption-isotherm relationship.

Considering a step increase in feed concentration in the liquid phase, if both the phase and sorption equilibria are of the favorable type, then their effects on concentration dependence of the equilibrium propagation velocity are coupled in the same direction, and thus, sharpening-type wave-propagation behavior is observed. Similarly, if both the phase and sorption equilibria are of the unfavorable type, then spreading-type wave-propagation behavior is observed. However, for cases where the phase and sorption equilibrium relationships are of opposite type (e.g. favorable-phase–unfavorable-sorption equilibria, or unfavorable-phase–favorable-sorption equilibria) the concentration waves may either sharpen or spread depending on relative concentration dependence of these equilibrium relationships. Furthermore, the relative concentration dependencies of the phase- and sorption-equilibrium relationships may be such that a concentration-dependent transition from tendency to sharpen towards tendency to spread (or vice versa) may be observed within a wave (as the concentration decreases from upstream end to downstream end of the wave). For comparable degree of nonlinearities in the phase and sorption equilibria, the nature of the phase-equilibrium relationship has the dominating effect on equilibrium propagation velocity since its influence on both the numerator and denominator of eq. (18) are coupled in the same direction. The effects of the nonlinearities in the phase- and sorption-equilibrium relationships on wave-propagation behavior are classified in Table 3.

Condition for stagnation of concentration waves

The equilibrium propagation velocity in eq. (17) defines a trajectory which can be written as

$$\Phi(C_L) = \frac{dz}{dt}. \tag{22}$$

For a liquid-phase disturbance, a representative trajectory can be constructed by integrating eq. (22) from $z = 0$ (for a gas-phase disturbance the integration should start from $z = L$) (Hwang and Helfferich, 1988):

$$t = \int_0^z \left\{ \frac{\theta_L(C_L)\left[1 + \left(\frac{\theta_G(C_L)h_G}{\theta_L(C_L)h_L}\right)\frac{dC_G^*(C_L)}{dC_L}\right]}{\left(\frac{u_L}{\varepsilon_L}\right) - \left(\frac{u_G}{\varepsilon_G}\right)\left(\frac{h_G}{h_L}\right)\frac{dC_G^*(C_L)}{dC_L}} \right\} dz. \tag{23}$$

Equation (23) reveals that, for the propagation of a disturbance introduced in the liquid phase, there may be an asymptotic limit corresponding to zero denominator if on the steady-state profile (zero denominator corresponds to infinite value of time,

Table 3. Effects of equilibrium isotherms on wave-propagation dynamics for a step increase in feed concentration

Type of phase (gas–liquid) equilibrium	Type of sorption (gas–solid or liquid–solid) equilibrium	Wave-propagation behavior
Linear	Linear	As introduced
Linear	Favorable	Sharpening
Linear	Unfavorable	Spreading
Favorable	Linear	Sharpening
Favorable	Favorable	Sharpening
Favorable	Unfavorable	*
Unfavorable	Linear	Spreading
Unfavorable	Favorable	*
Unfavorable	Unfavorable	Spreading

* Wave-propagation behavior depends on relative concentration dependence of the phase- and sorption-equilibrium isotherms. (Wave propagation may be of combined type, i.e. sharpening and spreading.)

which in turn, corresponds to the steady-state conditions) there exists $C_L(z, t = \infty)$ satisfying the following condition:

$$\frac{dC_G^*(C_L(z, t=\infty))}{dC_L} = \left[\frac{(u_G/\varepsilon_G)}{(u_L/\varepsilon_L)}\left(\frac{h_G}{h_L}\right)\right]^{-1}. \quad (24)$$

This condition means that the slope of the equilibrium curve [left-hand side of eq. (24)] is equal to the slope of the operating line [right-hand side of eq. (24), which is a ratio of molar fluxes of the liquid and gas phases]. This asymptotic propagation suggests a *stagnation point*; any disturbance becomes stagnant when approaching this condition.

The propagation dynamics of an exsorption column for a linear system is simple and independent of the background (steady-state) concentration profile: a disturbance will either travel through the entire exsorption column (if $\Phi > 0$) or be barred from entering the column (no stagnation can occur within the column, but also, no disturbance can go into the column if $\Phi \leqslant 0$). The propagation dynamics of an exsorption column for a nonlinear system, however, depends on the background concentration profiles (the liquid- and gas-phase concentration profiles, and also, adsorbent–loading profile) on which the disturbance propagates. Concentration-dependent equilibrium propagation velocity may vanish within the exsorption column leading to stagnation behavior (if the disturbance can enter the column).

Effect of the magnitude of step disturbance

Another characteristic of wave-propagation dynamics pertinent to nonlinear systems is the dependence of the stagnation behavior on the magnitude of the step with which the disturbance is introduced into the column. Under local-equilibrium conditions, a self-sharpening wave either sharpens during its travel and eventually becomes a discontinuous step in a sufficiently long column, or remains discontinuous if it was introduced as a step. In such a situation where a concentration wave travels as a discontinuous step, the differential material balance [eq. (17)] can be replaced with a difference-from material balance (Hwang and Helfferich, 1988), leading to the following *step velocity*:

$$\Phi_\Delta(C_L^- \mid C_L^+) = \left\{\frac{\left(\frac{u_L}{\varepsilon_L}\right) - \left(\frac{u_G}{\varepsilon_G}\right)\left(\frac{h_G}{h_L}\right)\frac{\Delta C_G^*}{\Delta C_L}}{\theta_L(\Delta)\left[1 + \left(\frac{\theta_G(\Delta)h_G}{\theta_L(\Delta)h_L}\right)\frac{\Delta C_G^*}{\Delta C_L}\right]}\right\} \quad (25)$$

where for case II wetting conditions of exsorption:

$$\theta_L(\Delta) = \left[1 + \left(\frac{1-\varepsilon}{\varepsilon_L}\right)\left(\frac{\rho_q}{\rho_L}\right)\left(\frac{\varepsilon_L}{\varepsilon}\right)\frac{\Delta q_L^*}{\Delta C_L}\right] \quad (26)$$

$$\theta_G(\Delta) = \left[1 + \left(\frac{1-\varepsilon}{\varepsilon_G}\right)\left(\frac{\rho_q}{\rho_G}\right)\left(\frac{\varepsilon_G}{\varepsilon}\right)\frac{\Delta q_G^*}{\Delta C_L}\right] \quad (27)$$

where for case I wetting conditions of exsorption:

$$\theta_L(\Delta) = \left[1 + \left(\frac{1-\varepsilon}{\varepsilon_L}\right)\left(\frac{\rho_q}{\rho_L}\right)\frac{\Delta q_L^*}{\Delta C_L}\right] \quad \theta_G = 1 \quad (28)$$

where

$$\Delta C_L = C_L^- - C_L^+, \quad \Delta C_G^* = C_G^*(C_L^-) - C_G^*(C_L^+)$$
$$\Delta q_L^* = q_L^*(C_L^-) - q_L^*(C_L^+),$$
$$\Delta q_G^* = q_G^*(C_G^*(C_L^-)) - q_G^*(C_G^*(C_L^+)) \quad (29)$$

where C_L^- and C_L^+ are the concentrations on the upstream and downstream sides of the step disturbance.

Considering the local equilibrium conditions for which these equations are derived, and the start-up of exsorption column with a step increase in feed concentration over a zero initial concentration profile and zero initial adsorbent–loading profile, the concentration of solute in the feed can be taken as C_L^-, which is the magnitude of the step disturbance. Since the concentration wave (step disturbance) propagates as a perfect discontinuity, under local equilibrium conditions, the downstream end of the wave has zero concentration which can be represented by C_L^+. Therefore, the condition for stagnation, in analogy to eq. (24), can be stated in difference as

$$\frac{\Delta C_G^*}{\Delta C_L} = \frac{C_G^*(C_L^-) - C_G^*(C_L^+)}{C_L^- - C_L^+} = \left[\frac{(u_G/\varepsilon_G)}{(u_L/\varepsilon_L)}\left(\frac{h_G}{h_L}\right)\right]^{-1}. \quad (30)$$

Hence, there may exist, depending on the phase-equilibrium relationship but not on the sorption-equilibrium relationship(s), a value of feed concentration C_L^- (magnitude of step disturbance) to an exsorption column which satisfies the condition for stagnation.

Comparison of the equilibrium theories of adsorption, extraction, and exsorption

The equilibrium theory of adsorption can be derived starting with the partial differential equation describing solute movement in the fluid phase and by making the local sorption-equilibrium assumption. The resulting propagation velocity of concentration waves is given by (Ruthven, 1984; Rhee *et al.*, 1986; Yang, 1987):

$$\Phi^{ads}(C) = \frac{(u/\varepsilon)}{\left[1 + \left(\frac{1-\varepsilon}{\varepsilon}\right)\left(\frac{\rho_q}{\rho}\right)\frac{dq^*(C)}{dC}\right]}. \quad (31)$$

The equilibrium theory of countercurrent extraction can be derived starting with the partial differential equation describing solute movement in the liquid and gas phases and by making the local phase-equilibrium assumption. The resulting propagation velocity of concentration waves is given by (Hwang, 1987;

Hwang and Helfferich, 1988):

$$\Phi^{ext}(C_L) = \left\{ \frac{\left(\frac{u_L}{\varepsilon_L}\right) - \left(\frac{u_G}{\varepsilon_G}\right)\left(\frac{h_G}{h_L}\right)\frac{dC_G^*(C_L)}{dC_L}}{1 + \left(\frac{h_G}{h_L}\right)\frac{dC_G^*(C_L)}{dC_L}} \right\}. \quad (32)$$

It should be noticed that, for $\theta_L = 1$ and $\theta_G = 1$, propagation velocity of exsorption [eq. (18)] reduces to propagation velocity of extraction [eq. (32)] and the stagnation conditions of exsorption [eq. (24) or (30)] and extraction are identical.

When eqs (31) and (32) are compared with eq. (18), it can be understood that wave-propagation dynamics of exsorption is not superposition of those of the adsorption and extraction. The propagation dynamics (sharpening or spreading wave-propagation behavior) of an exsorption column is affected by the nature (concentration dependence) of the phase equilibrium and the gas- and/or liquid-phase sorption equilibria. However, as it should be obvious from the numerator of eq. (18) [or from eq. (24)] the condition for stagnation of concentration waves is independent of the nature of the sorption equilibria. In an countercurrent exsorption column, stagnation of concentration waves may occur if and only if the phase-equilibrium relationship is of the favorable-type (if the disturbance can indeed enter the column). In a cocurrent exsorption column, the interstitial gas-phase velocity has the same direction (positive sign) as the liquid-phase velocity, and therefore, stagnant waves cannot develop [the denominator of eq. (23) is always positive and thus never vanishes]. Also, the effects of the background concentration profiles in the liquid, gas and the adsorbent phases on wave-propagation dynamics in an exsorption column is more complicated compared to extraction due to interactions of the phase- and sorption-equilibrium relationships as revealed by the equilibrium propagation velocity of exsorption [eq. (18)].

The conclusions reached on the basis of the equilibrium theory of the system can be further validated through numerical solution of the plug-flow versions of the non-equilibrium distributed-parameter models of exsorption column. These simulations studying the effects of the phase- and sorption-equilibrium relationships, magnitude of step disturbance, demonstrating the stagnation conditions, and providing comparisons among the three cases of wetting conditions in detail can be found elsewhere (Akman, 1991c; Akman and Sunol, 1992).

CONCLUSIONS

Equilibrium theory of exsorption predicts the most important aspects of propagation dynamics of mass fronts. It explicitly reveals the individual and relative contributions of the phase (gas–liquid) equilibrium and sorption (gas–solid and/or liquid–solid) equilibrium isotherms on propagation dynamics.

For a given set of operating conditions (phase velocities and phase holdups), the equilibrium theory of exsorption predicts that the criteria for either the development of stagnant wave fronts within an exsorption column (if the disturbance can enter the exsorption column) and the magnitude of a step disturbance with which the solute can enter the column are independent of the type (linear, favorable, unfavorable) and nature (concentration dependence) of sorption-equilibrium isotherm(s). Stagnation of concentration waves is possible, and the magnitude of a step disturbance is important, only if the phase-equilibrium isotherm is of favorable type (if the propagation velocity decreases with increasing axial position within a wave due to phase-equilibrium relationship).

If the concentration dependence of the phase- and sorption-equilibrium isotherms are known, the equilibrium theory of exsorption can be used in the design of the process and its control structures, in developing its operational policies, and in estimation of cycle times for a possible cyclic multi-column operation of exsorption.

NOTATION

a_G	gas–liquid interfacial area, cm^2/cm^3 bed
a_s	external surface area per volume of particle, cm^{-1}
C, C_G, C_L	mole fraction of solute in fluid, gas, and liquid phases
C_G^o, C_L^o	mole fraction of solute in gas and liquid feeds
C_L^-, C_L^+	mole fraction of solute on upstream and downstream sides of step disturbance
C_G^*	equilibrium mole fraction of solute in gas phase
E_{zG}, E_{zL}	axial dispersion coefficients in gas and liquid phases, cm^2/s
h_G, h_L	molar holdup of gas and liquid phases, mol/cm^3 bed
K_{OG}	overall mass-transfer coefficient, $mol/s\ cm^2$
K_{sG}^p, K_{sL}^p	particle/gas and particle/liquid mass-transfer coefficients, cm/s
L	bed length, cm
q_G^*, q_L^*	equilibrium adsorbent loadings from gas and liquid phases, mol/g
q_G, q_L	adsorbent loading in gas and liquid regions, mol/g
t	time, s
u_G, u_L	superficial gas- and liquid-phase velocities, cm/s
z	axial position, cm

Greek letters

ε	total bed voidage ($\varepsilon = \varepsilon_G + \varepsilon_L$)
ε_G, ε_L	volumetric gas- and liquid-phase holdups, cm^3/cm^3 bed
ρ, ρ_G, ρ_L	density of fluid, gas, and liquid phases, mol/cm^3
ρ_q	density of adsorbent phase, g/cm^3
Φ	equilibrium propagation velocity in exsorption, cm/s

Φ^{ads} equilibrium propagation velocity in adsorption, cm/s

Φ^{ext} equilibrium propagation velocity in extraction, cm/s

ω_G, ω_L propagation velocities in gas and liquid phases under local sorption-equilibrium conditions, cm/s

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