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Release model of alginate microcapsules containing volatile tea-tree oil

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ABSTRACT

We have prepared alginate calcium microcapsules containing tea tree oil and measured the release behavior. The release rate observed at different temperatures was almost constant with time. The data were analyzed by a theory for a model system consisting of encapsulated coexisting liquid and vapor phases. The theory predicts a polynomial-type release which is much more uniform than the exponential-type release appearing in conventional microcapsule systems and regarded as roughly constant release. The observed release curves were expressed well by the theoretical equation for the release, which supports the validity of the theory. From the fitting of the data to the theory, the time constant for vaporization in the core and that for permeation through the microcapsule membrane were determined. The activation energy for permeation through the membrane determined from the fitting parameters is much larger than that for vaporization.

1. Introduction

Essential oils are widely adopted into modern society because of their variety of bioactivity [1–5]. Above all tea tree oils and their extracts have been used as a botanical medicine in various forms over the centuries. In recent decades there has been lots of studies conducted with tea tree oils in dermatologic and oral treatments from a viewpoint of antimicrobial activities [6–9]. Since most bioactive components of tea tree oils are volatile, it is more effective to be used as an encapsulated entity in many cases. Microcapsulation has attracted increasing interests for variety of fields and is still developed further. One disadvantage of the conventional microcapsules is, however, the exponential-type release of the core materials [10–12]. It results from the release induced by the concentration gradient of the materials between the microcapsule core and the dispersing phase (environment). In the case of microcapsules containing volatile liquid such as tea tree oil, the volatile liquid phase and vapor phase coexist in the microcapsule core during the release process. Therefore, the release behavior is much different from the conventional one. In this study, we prepared alginate calcium microcapsules containing tea tree oil, measured the release behavior and analyzed it with a theory for a model system. The release rates observed at different temperatures were almost constant with time, and the release curves were well expressed by the theoretical equation for the release.

2. Experimental results

Sodium alginate (ELH2885) was purchased from Wako Pure Chemicals, Japan, and others were purchased from First Chemical, Taiwan. 2 mL of tea tree oil was poured into 20 mL of 1.0 wt% sodium alginate aqueous solution. 0.1 mL of Arlacel was added into it as a surfactant. The mixture was stirred with a homogenizer (HG-300D+K12S, Shuang-Tai, Taiwan) at 5000 rpm for 10 min to obtain an emulsion. Then 0.1% $CaCl_2$ aqueous solution was dripped into it and the mixture was stirred slowly for 120 min to make microcapsules with alginate wall membrane encapsulating the tea tree oil. The microcapsule suspension was washed with distilled water twice. Finally, the resultant alginate microcapsule samples were dried in a vacuum oven (TK30, Young-Chenn, Taiwan) at 30 °C overnight to evaporate remaining water on the microcapsule surface, and subsequently hardened by incubation at 37 °C. The encapsulation efficiency was defined as $E_{ff} = O_w/(O_w + W_0)$, where O_w is the weight of tea tree oil used for the preparation, and W_0 is the weight of microcapsules measured after complete evaporation of tea-tree oil at 120 °C for 1 h. The encapsulation efficiency was determined as 97.5%.

The particle size of the prepared microcapsules was determined using a particle size analyzer (MSS, Malvern Instruments, UK). Chloroform was used as a nonsolvent dispersion medium and the particles were mechanically suspended by magnetic stirring during the measurement. The average particle size of alginate microcapsules was determined as 0.43 ± 0.04 μm.

The release of tea tree oil from the microcapsules during an incubation process at different temperatures between 40 °C and 90 °C was traced by measuring the time course of the weight $W_m(t)$

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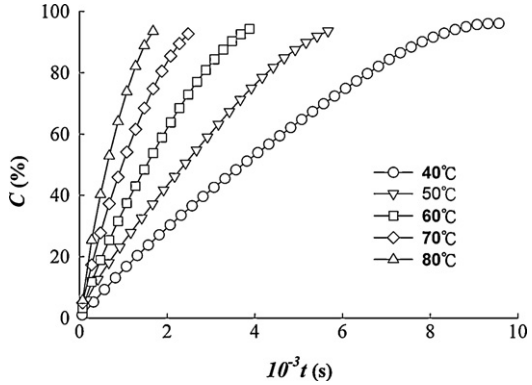

Fig. 1. Release curves for alginate microcapsules at different temperatures of 40 °C (circle), 50 °C (triangle-down), 60 °C (square), 70 °C (diamond), and 80 °C (triangle-up).

of the microcapsules placed on an Infrared Moisture Determination Balance (IMDB)(AD-4715, AND). Here, t is the incubation time. The temperature and the sample weight was measured continuously and recorded automatically. The oil release content was defined as $C(\%) = [(W_m(0) - W_m(t))/(W_m(0) - W_0)] \times 100$, where $W_m(0)$ denotes the weight of microcapsules measured at the initial state. Fig. 1 shows the release behavior at different temperatures.

3. Theoretical analysis and discussion

Fig. 2 shows an illustration of the release model. At the initial state the microcapsule core is completely filled with the release materials (liquid component). As time passes, a part of the liquid is evaporated and the microcapsule core consists of coexisting liquid phase and vapor phase. To describe the release from microcapsules containing volatile liquid (or solid) and coexisting vapor phase as shown schematically in Fig. 2, we use the following notation: V_0 and $V(t)$ are the volume of release materials at the initial state (volume of microcapsule core) and that at time t, respectively. S_0 and $S(t)$ are the surface area of release materials at the initial state (surface area of microcapsule core) and that at time t, respectively, $\rho(t)$, ρ_0 and $\bar{\rho}$ are the number concentrations of release material molecules in the vapor phase in the core at t, the saturated one in the vapor phase, and in the dispersing medium, respectively, and σ is the number density of release material molecules in the liquid phase.

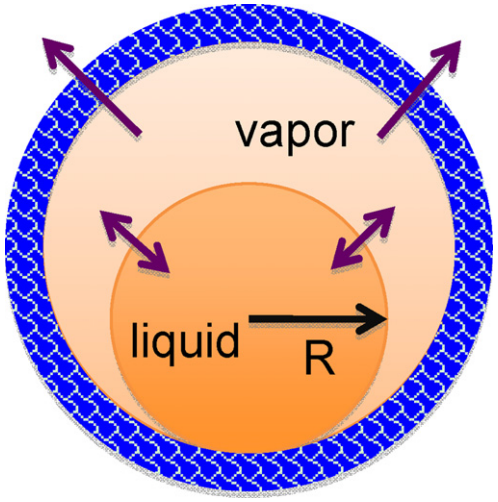

Fig. 2. Release model.

The flow of release material molecules per unit surface area through the microcapsule membrane and that from the liquid surface by vaporization are expressed, respectively, as:

$$j = k(\rho - \bar{\rho}) \tag{1}$$

and

$$J = \alpha(\rho_0 - \rho) \tag{2}$$

where k and α are positive constants. The time development of the number of the release material molecules in the vapor phase in the core and that in the liquid phase are then expressed, respectively, as:

$$\frac{d}{dt}[(V_0 - V(t))\rho(t)] = -S_0 j + SJ \tag{3}$$

$$\frac{d}{dt}(V\sigma) = -SJ \tag{4}$$

Since σ is constant and the inequality $\sigma \gg \rho \gg \bar{\rho}$ holds during the release process, substituting Eq. (1) into Eqs. (3) and (4), we have

$$V_0 \frac{d\rho}{dt} + \frac{dV}{dt}\sigma = -S_0 k\rho \tag{5}$$

$$\frac{dV}{dt}\sigma = -S\alpha(\rho_0 - \rho) \tag{6}$$

Assuming the shape of the liquid phase is a sphere and denoting the radius at the initial state and at time t as R_0 and $R(t)$, respectively (hence, $V_0 = (4/3)\pi R_0^3$, $V(t) = (4/3)\pi R^3(t)$, $S_0 = 4\pi R_0^2$ and $S(t) = 4\pi R^2(t)$), in terms of the functions R and ρ we rewrite the simultaneous basic equations (5) and (6) as:

$$\frac{4}{3}\pi R_0^3 \frac{d\rho}{dt} + 4\pi R^2 \sigma \frac{dR}{dt} = -4\pi k R_0^2 \rho \tag{7}$$

$$\sigma \frac{dR}{dt} = -\alpha(\rho_0 - \rho) \tag{8}$$

Introducing the scaled variables, $\tilde{\rho} = \rho/\rho_0$, $\tilde{R} = R/R_0$ and $\tilde{t} = t/\tau$ with $\tau \equiv \sigma R_0/(\alpha\rho_0)$, and a non-dimensional parameter $\lambda = \alpha/k$, we have the scaled equations corresponding to Eqs. (7) and (8) as:

$$\frac{d\tilde{R}}{d\tilde{t}} = -\frac{1}{1 + \lambda\tilde{R}^2}\left(1 + \frac{\rho_0}{\sigma}\lambda\frac{d\tilde{\rho}}{d\tilde{t}}\right) \tag{9}$$

$$\tilde{\rho} = 1 + \frac{d\tilde{R}}{d\tilde{t}} \tag{10}$$

Since $\frac{\rho_0}{\sigma} \ll 1$, the above simultaneous equations are decoupled and Eq. (9) is rewritten as:

$$\frac{d\tilde{R}}{d\tilde{t}} = -\frac{1}{1 + \lambda\tilde{R}^2} \tag{11}$$

From Eqs. (10) and (11), the scaled concentration $\tilde{\rho}$ is expressed as:

$$\tilde{\rho} = \frac{\lambda\tilde{R}^2}{1 + \lambda\tilde{R}^2} \tag{12}$$

Therefore, $\tilde{\rho}$ reaches the saturated value ($\tilde{\rho} \cong 1$) for large λ whereas the release material concentration in the vapor phase vanishes ($\tilde{\rho} \approx 0$) for small λ. This means that the release from the microcapsules is limited by the vaporization from the liquid phase in the core when λ is small and the permeation through the microcapsule membrane when λ is large.

We obtain the solution of Eq. (11) as:

$$\tilde{R}(\tilde{t}) + \frac{1}{3}\lambda\tilde{R}^3(\tilde{t}) - \left(1 + \frac{1}{3}\lambda\right) = -\tilde{t} \tag{13}$$

where we choose the initial condition $R(0) = R_0$ since the core area is entirely occupied by the release material liquid at the initial stage $t = 0$.