Kinetics of molecular encapsulation of 1-methylcyclopropene into α-cyclodextrin

T. L. Neoh, K. Yamauchi, H. Yoshii * and T. Furuta *
4-101 Koyama Minami, Tottori Tottori University - Tottori, Japan
(neoh@bio.tottori-u.ac.jp)

Introduction

1-Methylcyclopropene (1-MCP), a colorless gas at standard temperature and pressure, is an ethylene inhibitor which has been reported of its satisfactory efficiency in blocking ethylene receptors and thus preventing ethylene effects in a broad range of fruit, vegetables and floriculture crops. Physiological effects of 1-MCP have been studied on a wide range of fruits, vegetables and ornamental crops including apple (Watkins et al. (2000)), avocado (Adkins et al. (2005)), broccoli (Able et al. (2002)), lettuce (Wills et al. (2002)), carnation (Sisler et al. (1996)), etc.
Although 1-MCP is currently being commercialized in the form of inclusion complex with α-cyclodextrin (α-CD), the information about the encapsulation behavior and release characteristic of this particular inclusion complex is, to our knowledge, hardly available at the present. In this research, we aim to investigate the encapsulation of 1-MCP gas into α-CD cavity. Besides, the stability of the inclusion complex was also studied based on heat dissociation.

Materials and Methods

1-MCP was synthesized in the form of lithium salt by reacting 2.4 mL of 3-chloro-2-methylpropene (98%) with 21.42 g of lithium diisopropylamide (LDA) (30 wt% suspension in mineral oil) in a closed 60-mL amber vial. 3-chloro-2-methylpropene was added drop wise to lithium diisopropylamide over 60 min with gentle mixing. After addition, mixing was performed for another 30 min to ensure complete reaction between the two chemicals. Lithium salt of 1-MCP was collected as a suspension in mineral oil. Vacuum was pulled on the suspension to approximately 0.1 kPa to eliminate volatile impurities. The suspension was stored at -25 °C until use.

Vacuum was pulled to about 0.27 kPa in the reaction bottle containing 100 g distilled water (Figure 1(a)). Then, the previously thawed liquid suspension of lithium salt of 1-MCP was injected into the reaction bottle using a 20-mL syringe (Figure 1(b)). Agitation was performed to promote complete release of 1-MCP for about 15 min. The 1-MCP gas would evaporate and accumulate in the headspace of the reaction bottle. Meanwhile, saturated α-CD solution (87.3 mM) was prepared in the encapsulation bottle based on 100 g distilled water and vacuum was pulled to about 0.27 kPa (Figure 1(c)). The reaction and encapsulation bottles were connected to each other with a Teflon tube through the valves installed on the screw-cap of each bottle as illustrated in Figure 1(d). Circulation of headspace in both bottles was enhanced with mini-fans. 1-MCP was transferred from the reaction bottle to the encapsulation bottle by opening the valves. After that, both valves were closed and nitrogen was filled into the reaction bottle to create atmospheric pressure. The valves were then re-opened to equalize the pressure in both bottles. This procedure was repeated until the pressure of both bottles reached atmospheric pressure. Finally, the encapsulation bottle was separated and encapsulation was promoted by agitation of α-CD solution at 200 rpm (Figure 1(e)). Encapsulation was performed at 20 °C. Agitation of headspace was performed through out the encapsulation process. At the end of the encapsulation process, α-CD solution that contained inclusion complex as precipitate was centrifuged at 3000 rpm for 15 min and the inclusion complex was separated and dried *in-vacuo* for 24 h at room temperature. During encapsulation process, the depletion of 1-MCP in the headspace of encapsulation bottle was monitored by gas chromatography

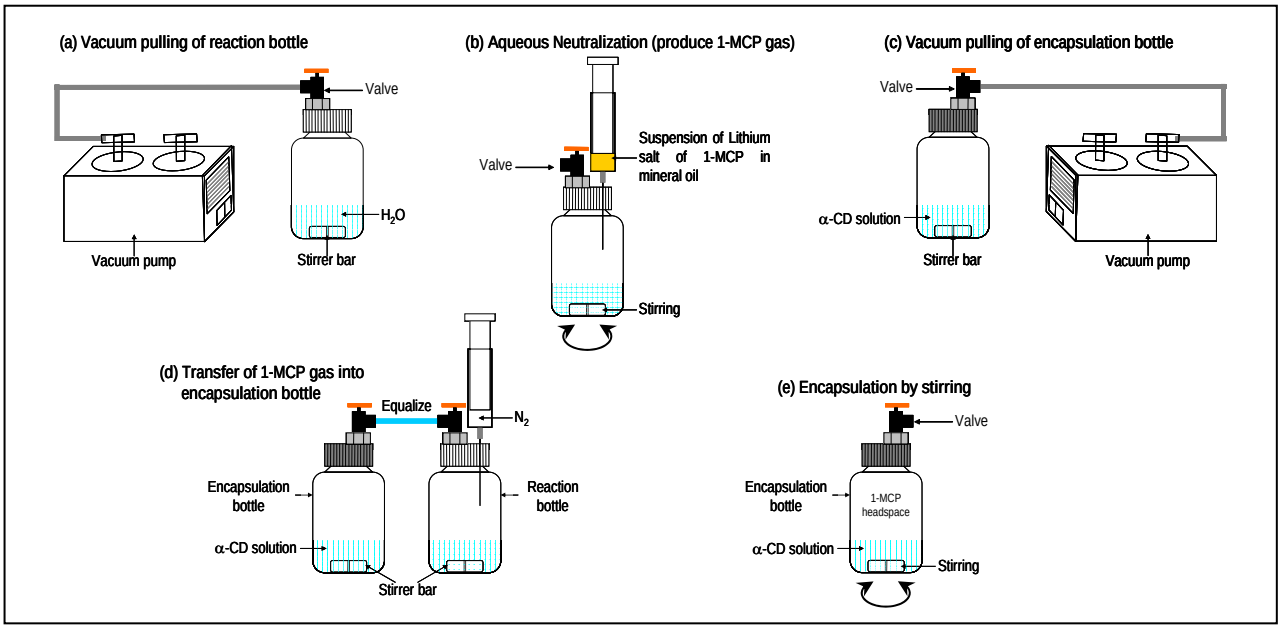

Figure 1. Schematic diagram of encapsulation of 1-MCP into aqueous α-CD.

as described below. The depletion rate of 1-MCP during the initial stage of encapsulation is postulated to reflect the apparent encapsulation rate of 1-MCP into α-CD cavity.

The inclusion ratio of 1-MCP is presented in a dimensionless term defined as the molar ratio of the included 1-MCP to α-CD. Approximately 10 mg of inclusion complex was weighed into a 20-mL GC vial. The vial was then closed with a butyl rubber stopper. Roughly 3 g of distilled water was injected into the vial and mixing was performed for 5 min to ensure dissolution of the inclusion complex. One tenth of a milliliter of the headspace was analyzed with the GC-2010 gas chromatograph (Shimadzu Corp., Kyoto, Japan) fitted with the ULBON HR-1 column (30 m L x 0.53 mm I.D. x 5 µm film) (Shinwa Chemical Industries, Ltd., Kyoto, Japan) and a flame-ionization detector. The injection port and detector temperatures were set at 110 and 210 ºC, respectively. The initial column temperature was 40 °C and the final temperature was 100 °C. Quantification of 1-MCP was accomplished using an external standard protocol (Jiang et al. (1999)). The isobutylene gas standard of 100 ppm concentration (Sumitomo Seika Chemicals Co. Ltd., Osaka, Japan) was used. It was presumed to have a response factor similar as 1-MCP.

Thermogravimetric (TG) curves were recorded on the EXSTAR 6000 TG/DTA (TG/DTA 6200, SII Nano Technology Inc., Tokyo, Japan) equipped with the Muse Measurement software, Version 3.7 (SII Nano Technology Inc.). Samples of 10±0.5 mg were weighed into aluminum pans for analysis at a heating rate of 5 ºC/min from 30 to 260 ºC in nitrogen atmosphere. Differential scanning calorimetry (DSC) was performed on the inclusion complex using the EXSTAR 6000 DSC (DSC 6220, SII Nano Technology Inc.) following the method identical to that in TG analysis. The aluminum pans were also left unsealed to simulate the sample condition during TG analysis. Data were analyzed using the Muse Measurement software, Version 3.7.

IR spectra of the uncomplexed α-CD and 1-MCP/α-CD complex were recorded using the Shimadzu FTIR-8300 Spectrophotometer (Shimadzu Corp., Kyoto, Japan) equipped with HYPER-IR software. The KBr pellet method was employed and measurements were performed at room temperature. Mixtures of 100 mg of KBr and 6 mg of either uncomplexed α-CD or 1-MCP/α-CD complex were pelletized at a hydrostatic pressure of 6-7 ton cm^{-2} for approximately 1 min. The scanning range was set at 400-4000 cm^{-1} and 20 scans were collected with a spectral resolution of 4.0 cm^{-1}.

Results and Discussion

Figure 2 shows the depletions of 1-MCP in encapsulation systems with different initial headspace concentrations of 1-MCP. The depletions of 1-MCP went through an almost similar path, regardless of the initial concentration of 1-MCP. Since α-CD concentration is enormously greater than that of 1-MCP, the whole encapsulation reaction could be approximated by a pseudo-first order reaction with respect to the aqueous concentration of 1-MCP.

Prominent IR absorptions were reported at wavenumbers of 693.3, 920.9, 957.0, 1028.9, 1056.8, 1150.4, 1394.7, 1440.1, 1476.3, 1780.0, 2884.1, 2912.1, and 2964.8 cm^{-1} by Maier et al. (2000). Two tiny absorption peaks at 1780.0 and 2912.1 cm^{-1}, which were not observable in the IR spectrum of uncomplexed α-CD, were found in the IR spectrum of the inclusion complex (Figure 3). Other than these two absorption peaks, the IR spectra of both uncomplexed α-CD and inclusion complex were almost similar suggesting that 1-MCP is encapsulated within α-CD's cavity rather than being chemically bonded to it.

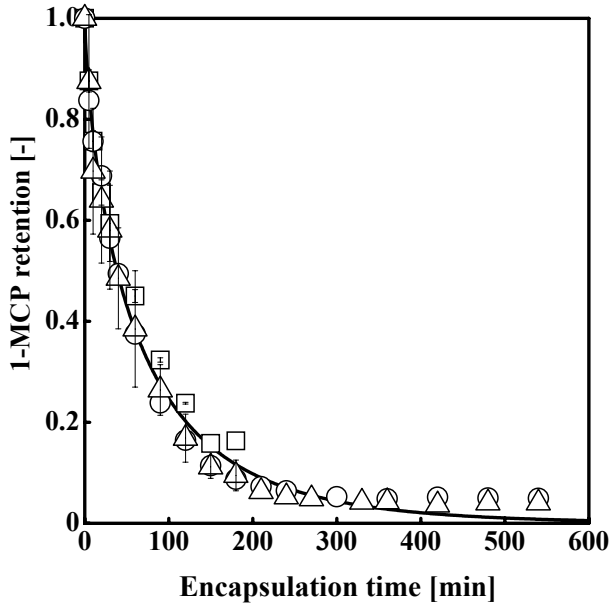

Figure 2. 1-MCP retention during encapsulation process. Encapsulation was carried out at initial 1-MCP headspace concentrations of 40,000 ppm (□), 80,000 ppm (○), and 100,000 ppm (Δ).

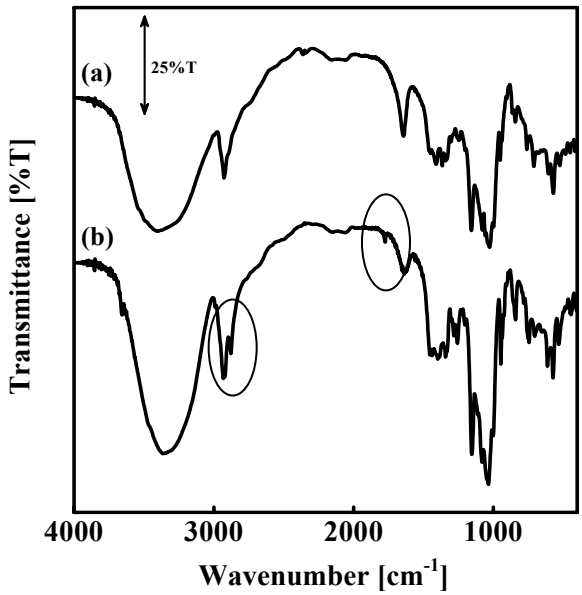

Figure 3. FTIR spectra of (a) uncomplexed α-CD and (b) 1-MCP/α-CD complex.

Figure 4 shows the thermogravimetric curves of uncomplexed α-CD and 1-MCP/α-CD complex. The initial weight decline in both curves could be attributed to the evaporation of water molecules from the samples. As the second decay happened only in the TG curve of the inclusion complex, commencing at around 119 ºC, the dissociation of 1-MCP from α-CD may plausibly account for the decay. The TG results were used to calculate the inclusion ratio of 1-MCP in α-CD.

Two heat absorption troughs are observed in the DSC curve of 1-MCP/α-CD complex (Figure 5). Referring to the TG curves, the first one may affirmatively be corresponding to the loss of water molecules from the inclusion complex sample. The second trough, found between 110 to 230 ºC, could positively be attributable to the dissociation of 1-MCP from the sample. The trough area was

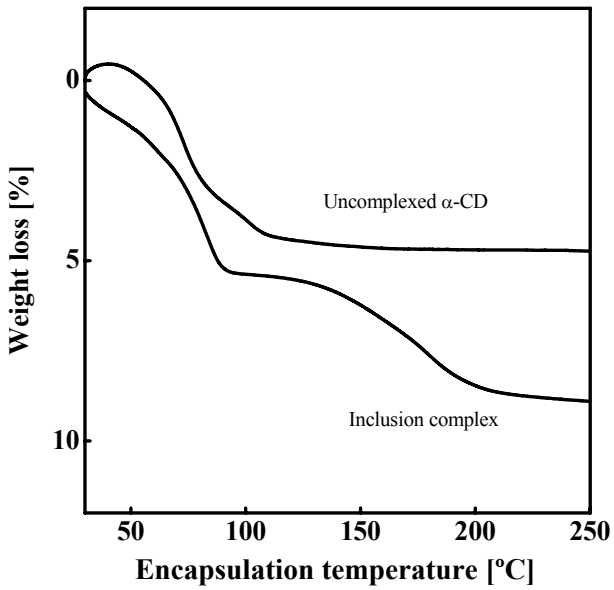

Figure 4. TG curves of uncomplexed α-CD and 1-MCP/α-CD complex.

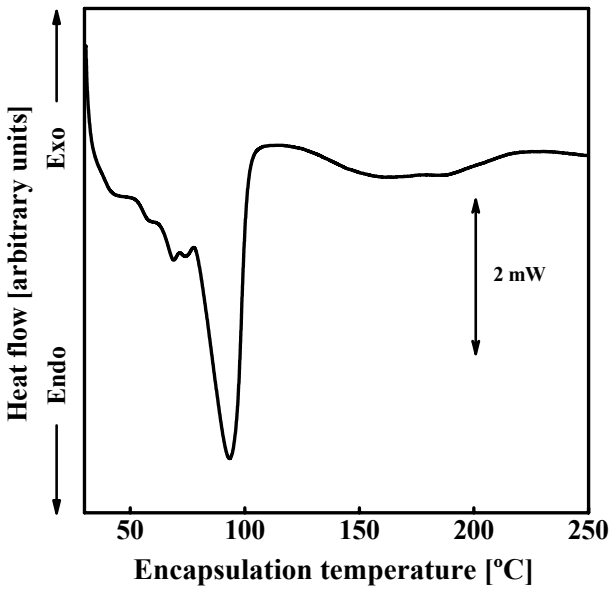

Figure 5. DSC curve of inclusion complex. The broad peak between 110 – 230 °C in the DSC curve was attributed to the dissociation of 1-MCP from α-CD.

computed, yielding the dissociation enthalpy of 1-MCP from α-CD at around 44 kJ/mol 1-MCP.

Conclusions

The encapsulation of 1-MCP into α-CD approximated a pseudo-first order reaction with respect to aqueous concentration of 1-MCP. The dissociation enthalpy of 1-MCP from α-CD was estimated at 44 kJ/mol 1-MCP.

References

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