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Preparation of Large Size Microcapsules Containing Tri-*n*-octylamine by *In situ* Polymerization Combined with a Gel Inclusion Method and Their Extraction Behavior

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Large size microcapsules containing tri-*n*-octylamine (TOA) with a diameter of larger than 2 mm were prepared by *in situ* polymerization with a gel inclusion of an organic droplet. A copolymer of styrene and divinylbenzene was used as the capsule wall material. When the concentration of TOA was high, the structure of the microcapsules was mono-cored with a thin wall and large cavity. However, at low TOA concentration, the structure changed to a matrix type filled with the copolymer. The TOA content in the microcapsules increased linearly with the initial TOA concentration in the organic phase until 60wt%. The extraction of acetic acid into the microcapsules was successfully carried out. It was possible to reuse the microcapsules 4 times and the extracted amount of acetic acid into the microcapsules was constant during their reuse.

1. Introduction

Solvent extraction processes have a high selectivity and are easy to scale-up, but solvent extraction uses large amounts of organic solvents which may adversely affect the environment and the human body. Solvent extraction also has some problems in that the phase separation of organic and aqueous phases is difficult and extractants and/or organic solvents are lost by being dissolved in the aqueous phase. To solve

these problems, the immobilization of the extractant [1-4] and microencapsulation of the extractant have been investigated [5-13]. Microcapsules encapsulating extractants which have been applied in solvent extraction systems are expected to be effective separation media for various substances such as metals [5-13], organic acids [14-16], antibiotics [17, 18], and environmental hazardous substances [19, 20], because of the high separation properties of the encapsulated extractant, which has been demonstrated in the solvent extraction system, and because of the high capacity for the extracted chemicals in their internal core.

Microcapsules are usually small particles with a size range of several 10 um – several 100 um. Hence, there are some problems which can cause harm to the human body and the environment by their ability to form dust, pipe blocking by aggregation of microcapsules in the plant and practical handling difficulties of the microcapsules due to their small size. If microcapsules having several millimeter size are prepared, these problems would be solved and the large size microcapsules could be used in the same applications as ion-exchange resins. Large size microcapsules are difficult to prepare by the *in situ* dispersion polymerization method because large droplets of the organic phase are quite unstable and readily coalesce. In this study, a large droplet of an organic phase containing tri-*n*-octylamine (TOA) and monomers of the wall material were included in a sodium alginate gel particle. Thereafter *in situ* polymerization of the droplet of the organic phase was carried out to obtain large size microcapsules containing TOA. The effect of the preparation conditions such as the TOA concentration in the organic phase, the concentration and composition of the styrene and divinylbenzene as the wall material in the organic phase, and the toluene diluents concentration in the organic phase on the structure of the microcapsules and the entrapment efficiency of TOA into the microcapsules were investigated. The extraction properties of acetic acid into the microcapsules and the durability of the microcapsules in the extraction process were also investigated.

2. Experimental

2.1 Reagents

Monomeric styrene and divinylbenzene (DVB) were purchased from Wako Pure Chemicals Co. and purified by distillation under nitrogen at reduced pressure. The distilled monomers were stored in a refrigerator until use. 2,2'-Azobis(2,4-dimethyl valeronitrile) (ADVN) was purchased from Wako Pure Chemical Co. and used as received. Tri-*n*-octylamine (TOA) obtained from Wako Pure Chemical Co. was used as the extractant without further purification. Reagent grades of toluene and sodium alginate, acetic acid, calcium chloride, sodium hydroxide, 0.1 mol/l HCl standard solution, phenolphthalein and bromocresol green were also purchased from Wako Pure Chemical Co. and used as received.

2.2 Preparation of large size microcapsules

A schematic of the preparation process for the large size microcapsules containing TOA by *in situ* polymerization with a gel inclusion of an organic droplet is shown in **Fig .1**. The organic phase consisted of

styrene, DVB, TOA, ADVN and toluene as the diluent. The weight ratio of styrene to DVB was kept at 1:1 and the concentration of ADVN was 0.50 wt% in the organic phase. Droplets of the organic phase were introduced into the sodium alginate aqueous solution using a coaxial cylindrical double glass nozzle as shown in **Fig. 2**. Each droplet of sodium alginate entrapping an organic droplet was added in a 10 wt% calcium chloride aqueous solution so as to form an alginic acid gel by complexation with the calcium ion. After gelation, alginate gel particles, each entrapping an organic droplet, were collected by filtration, added to distilled water in a round bottomed separation flask, in a previous paper [11], and then heated at 333K with stirring at 160rpm for 20 hours under a nitrogen atmosphere to carry out the *in situ* polymerization. After polymerization, the gel particles entrapping a polymer microcapsule containing TOA were filtered and put into a buffer solution of 0.1 mol•dm^{-3} K_2HOP_4-KH_2PO_4 at pH 7.0 to remove the calcium alginate film on the polymer microcapsule. The polymer microcapsules containing TOA were dried under normal room conditions.

2.3 Observation and analysis of large size microcapsules

The morphologies of the microcapsules were observed by scanning electron microscopy (Hitachi S-4100M, SEM) and a digital microscope (KEYENCE VH-8000). The internal structure of the microcapsules was examined by cross-sectioning of the microcapsules. The diameter of the microcapsules was measured from SEM photography using USB Digital Scale 1.0J software (SCALAR).

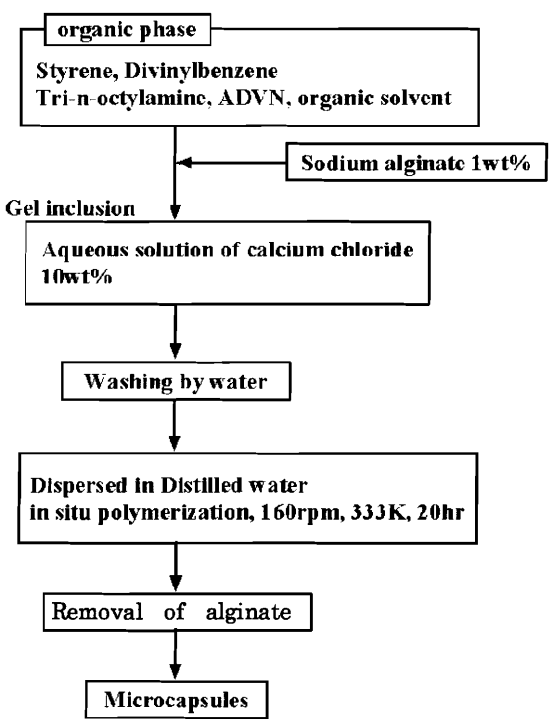


Fig. 1 Preparation schematic for large size microcapsules containing tri-*n*-octylamine (TOA) by *in situ* polymerization using a gel inclusion method.

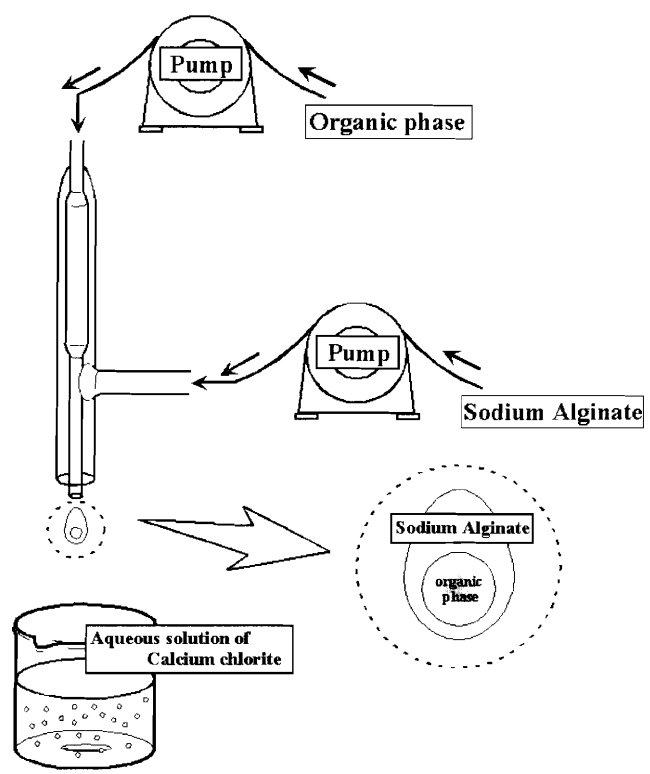


Fig. 2 Schematic illustration of the gel inclusion method using a coaxial cylindrical double glass nozzle.

In order to determine the amount of TOA entrapped in the microcapsules, the microcapsules were added to ethanol to elute TOA from the microcapsules, and the concentration of TOA in the ethanol solution was measured by titration with a 0.1 mol•dm^{-3} HCl aqueous solution using bromocresol green as the indicator. The amount of TOA per 1.0 g of the microcapsules, E, was calculated using the following equation;

$$E = \frac{C_{HCl} \times V_{HCl} \times M_{TOA} \times V_{Eth}}{V'_{Eth} \times W_{cap}} \qquad [g_{-TOA} / g_{-MC}] \qquad (1),$$

where C_{HCl}, V_{HCl}, M_{TOA}, V_{Eth}, V'_{Eth}, and W_{cap} are the concentration of HCl, the titrant volume, the molecular weight of TOA, the ethanol volume used for elution of TOA, the ethanol volume used for the titration and the weight of the microcapsules used for the elution, respectively.

2.4 Extraction of organic acid into large size microcapsules

The microcapsules contained TOA were added to an aqueous acetic acid solution (0.1 mol•dm^{-3}) and were shaken for 48 hour. The concentration of acetic acid in the aqueous solution at given time intervals was measured by titration with an NaOH aqueous solution using phenolphthalein as the indicator. The molar amount of acetic acid extracted into 1.0 g of the microcapsules, $C_{A,MC}$, was calculated using the following equation;

$$C_{A,MC} = \frac{(C_{A,aq,0} - C_{A,aq}) \times V_{A,aq}}{W_{cap}} \qquad [mol / g_{-MC}] \qquad (2),$$

where $C_{A,aq,0}$, $C_{A,aq}$ and V_A are the initial concentration of acetic acid, the concentration of acetic acid after extraction, the volume of acetic acid solution used for the extraction, respectively. In order to compare the extraction properties of TOA entrapped in the microcapsules with that in the solvent extraction system, the apparent association order of the complex of TOA with acetic acid, Z, was calculated using the following equation;

$$Z = \frac{(C_{A,aq,0} - C_{A,aq}) \cdot V_{A,aq}}{C_{B,MC,0} \cdot W_{cap}} \qquad [-] \qquad (3)$$

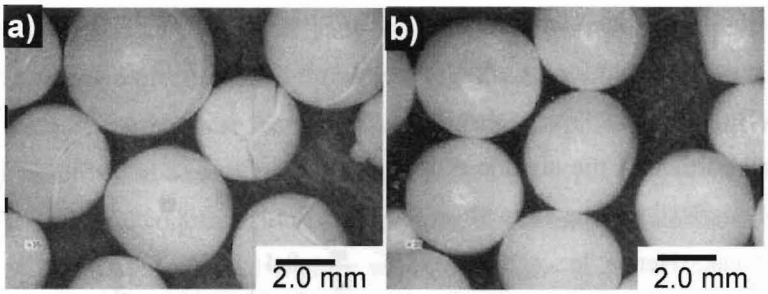
where $C_{B,MC,0}$ is the moles of TOA in 1.0 g of the microcapsules.

To determine the reusability of the microcapsules, the extraction was carried out using 50x10^{-3}dm^3 of 3.0 mol•dm^{-3} acetic acid solution and 5.0 g of the microcapsules, and then the back-extraction was carried out using 50x10^{-3}dm^3 of a 1.0 mol•dm^{-3} NaOH aqueous solution. After back-extraction, the microcapsules were used for extraction again. These processes were repeated several times.

3. Results and Discussion

3.1 Preparation of large size microcapsules containing TOA

The *in situ* polymerization of the droplet of the organic phase entrapped in the alginate gel particles was carried out successfully and the solidification of the organic phase in the gel particle was also successful. However, when the microcapsules were dried under room conditions after *in situ*



C_{st} = 35wt%, C_{DVB} = 35wt%, C_{TOA} = 30wt%

Fig. 3 Microphotographs of the large size microcapsules prepared at C_{TOA}=30wt%. a) dried with the alginate film. b) dried after removing the alginate film.

polymerization, many large cracks were formed on the surface of the microcapsules as shown in Fig. 3(a). These cracks were considered to be caused by shrinking of the calcium alginate film on the surface of the microcapsules during the drying process. Hence, the removal of the calcium alginate film from the surface was carried out by soaking the microcapsules in a buffer solution of 0.1 mol/l K_2HPO_4-KH_2PO_4 at pH 7.0 for several hours. The buffer solution can dissolve the calcium alginate gel by the formation of calcium phosphate which has a very low solubility in water. After drying of the microcapsules after removal of the alginate film, no cracks were observed on the surface as shown in Fig. 3(b). The removal of the alginate film is required to produce microcapsules with no cracks. The concentrations of TOA as the extractant and toluene as the diluent in the organic phase were changed to check for structural change, TOA entrapment and the extraction properties of the microcapsules.

3.2 Effect of the TOA concentration on the preparation of large size microcapsules

The microcapsules were prepared at various TOA concentrations in the organic phase. The SEM photographs of the microcapsules which were dried without removal of calcium alginate on the surface of the microcapsules are shown in Fig. 4. Shrinking of the alginate thin film was observed on the capsule surfaces. The microcapsules prepared at 0 – 30 wt% of TOA and filled with the copolymer of styrene and DVB, had no inside voids or pores, and the microcapsules were very strong. No leakage of TOA was observed onto the filter paper after preparation of the microcapsules.

The microcapsules prepared at 45 – 60 wt% were

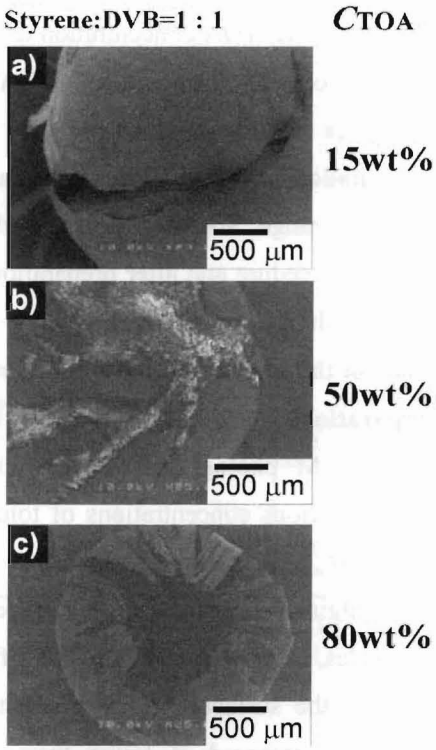


Fig. 4 SEM photographs observed from the upper side of the large size microcapsules prepared at C_{TOA}= 15, 50 and 80 wt%.

filled with small particles of the copolymer. This suggests that TOA is a poor solvent for the copolymer of styrene and DVB. The copolymer would be precipitated as a small particle in the organic droplet during the in situ polymerization. The strength of the microcapsules was weak. Hence leakage of TOA from the microcapsules was observed.

The microcapsules prepared at higher concentrations, 70 – 90 wt%, had a core-shell structure which had a thin shell film of the copolymer and a large void filled with TOA at the center of the microcapsules. The strength of the microcapsules was very weak and many broken microcapsules were observed by SEM as shown in Fig. 4 c). Severe leakage of TOA was also observed. The amount of wall material would be insufficient to form a capsule wall with sufficient strength.

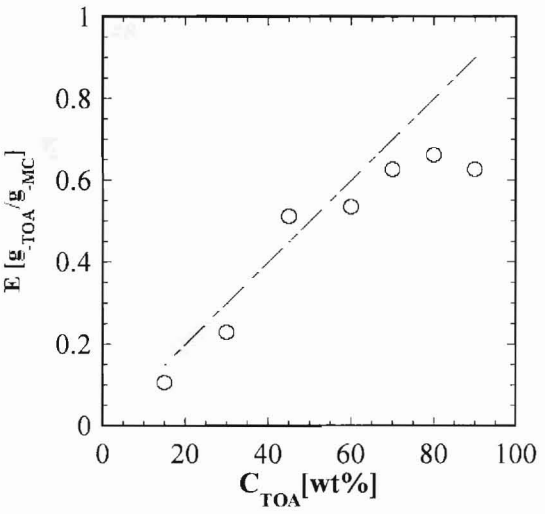


Fig. 5 Effect of TOA concentration in the organic phase on the content of TOA in 1g of the microcapsules. Styrene:DVB=1:1.

The content of TOA in 1g of the microcapsules, E, prepared at various initial TOA concentrations in the organic phase were plotted against their concentrations as shown in Fig. 5. The values of E increased linearly with initial TOA concentration until 60 wt%. However, at higher TOA concentrations the increase in E was reduced. Leakage of TOA from the microcapsules was observed on the filter paper after the preparation of the microcapsules in this concentration range. So, TOA was leaked during the preparation procedure and after preparation due to the lack of strength of the microcapsule.

3.3 Effect of the toluene concentration on the preparation of large size microcapsules

The SEM photographs of the microcapsules prepared at various concentrations of toluene and 15 wt% of TOA, which were dried after removal of calcium alginate from the surface of the microcapsules, are shown in Fig. 6. No difference was observed on the surface and inner structures of the microcapsules prepared at lower than 20 wt% of toluene in the organic phase. The microcapsules prepared at 40 wt% of toluene had many wrinkles on

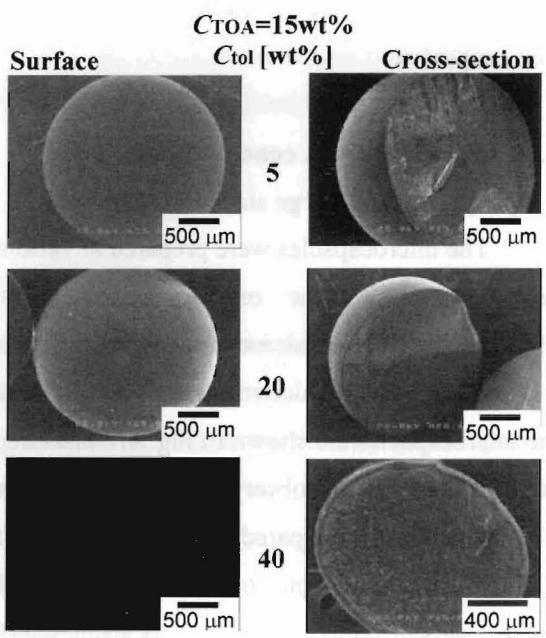


Fig. 6 SEM photographs of the surface and cross section of the microcapsules prepared at various toluene concentrations and 15 wt% of TOA in the organic phase. Styrene:DVB = 1:1.

the surface and a brittle inner structure with many small voids. Toluene was vaporized from the organic droplet during the *in situ* polymerization, and then shrinking of the organic droplets took place thus forming the wrinkles on the surface. Furthermore the vaporization of toluene produced small voids and pores inside the microcapsules as described in a previous paper [11].

The effect of the toluene concentration in the organic phase on the diameter of the microcapsules is shown in Fig. 7. The diameter decreased slightly with an increase in the concentration of toluene. This suggests that the shrinking of the organic droplet was due to the vaporization of toluene and the degree of shrinking became large with an increase in toluene concentration.

3.4 Extraction of acetic acid by large size microcapsules containing TOA

The extraction of acetic acid was carried out using microcapsules prepared at 30 wt% TOA or 30wt% TOA and 20 wt% toluene in the organic phase. The amounts of acetic acid extracted into the microcapsules were plotted against the extraction time as shown in Fig. 8. The amount of acetic acid extracted increased with time and reached constant values denoting extraction equilibrium, after 6 hr. The microcapsules prepared with the addition of toluene had higher extraction rates compared to those without the addition of toluene. The presence of toluene leads to the formation of micropores in the wall of the microcapsule on vaporization of the toluene during the *in situ* polymerization [11]. Hence extraction would occur easily through these micropores. In spite of the large size of the microcapsules which is around 2-3 mm, the extraction of acetic acid reached to equilibrium in a relative short time compared with the extraction of propionic acid by small size microcapsules containing TOA with a diameter of 200-400 μm as reported in a

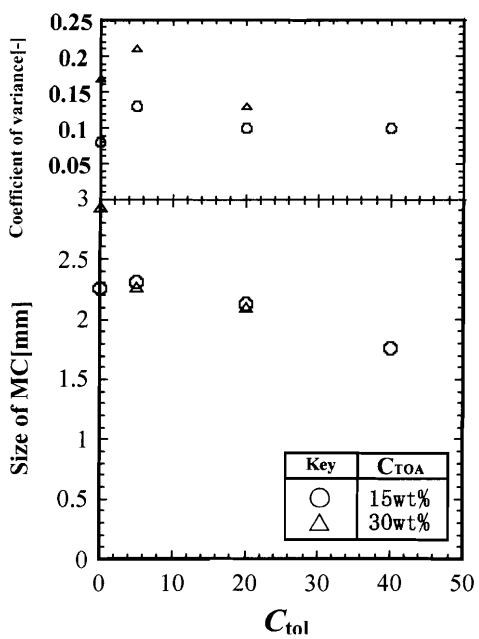


Fig. 7 The effect of toluene concentration on the diameter of the microcapsules prepared at 15 and 30 wt% of TOA in the organic phase. Styrene:DVB = 1:1.

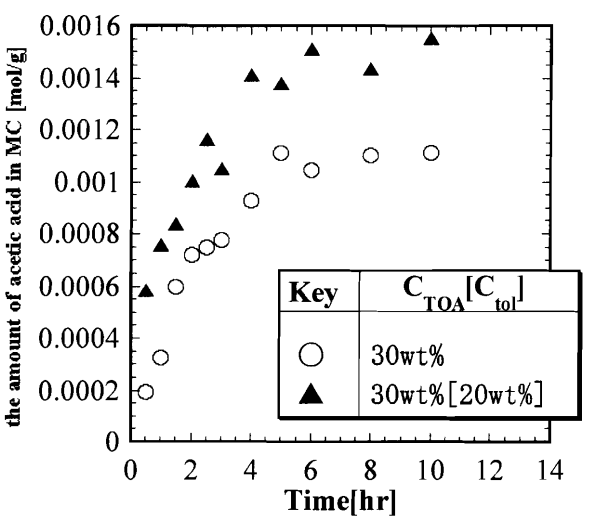


Fig. 8 Relationship between the amounts of acetic acid extracted into the microcapsules and the extraction time.

previous paper in which equilibrium was reached only after 2 – 6 hr depending on the concentration of the microcapsules used for the extraction [22]. In the case of the extraction of palladium (II) by small size microcapsules with diameters of less than 25 μm, the extraction rate is affected by the diameter of the small microcapsules and the diffusion of the extraction complex in the capsule wall is estimated to be the rate determining step [12]. However, in a case of acetic acid extraction by the large size microcapsules, the diameter of the microcapsules did not cause a serious decrease in the extraction rate. Further investigation of the kinetics of the extraction of acetic acid by the large size microcapsules is required.

The extraction of acetic acid by the large size microcapsules was carried out at various initial acetic acid concentrations. The relationship of the amount of acetic acid extracted in the microcapsules and the equilibrium concentration of acetic acid in the aqueous phase is shown in Fig. 9. The extracted amount of acetic acid in the microcapsules increased with the concentration of acetic acid in the aqueous phase depending on the concentration of TOA in the microcapsules. The amount of acetic acid extracted was the same when the TOA concentration was 30 wt% even though the toluene concentration was different at 5 or 20 wt%. In order to clarify this extraction property, the apparent association order of the complex of TOA with acetic acid, Z, was plotted against the concentration of acetic acid as shown in Fig. 10. The values of Z increased with the concentration of acetic acid and reached a value of 6. No effect of TOA on the plot was observed and the results at different TOA concentrations were plotted on the same line. Thus acetic acid extraction by TOA entrapped in the large size microcapsules is the same as that in the solvent extraction system in which the value of Z is plotted on the same line independent of the concentration of TOA and is only affected by the nature of the organic solvent [21]. Hence TOA entrapped in the large size microcapsules shows the same extraction properties as that of the solvent extraction system.

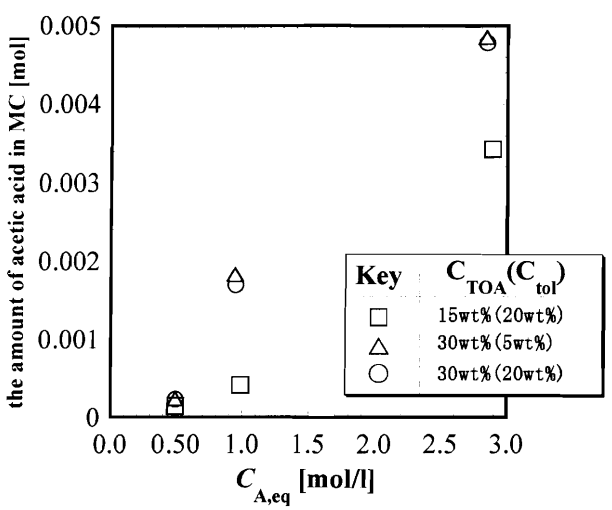


Fig. 9 Relationship between the amounts of acetic acid extracted in the microcapsules and the concentration of acetic acid in the aqueous phase. Styrene:DVB = 1:1.

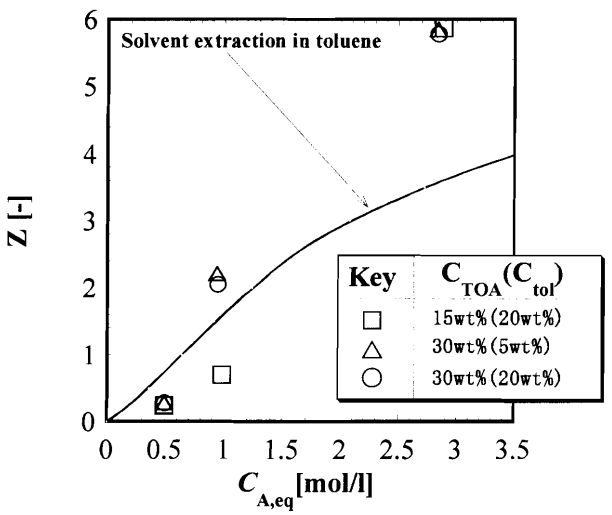


Fig. 10 Relationship between the value of Z and the concentration of acetic acid in the aqueous phase. Styrene:DVB = 1:1.

3.5 Durability of large size microcapsules containing TOA

Large size microcapsules prepared at 30 wt% TOA and 20 wt% toluene were repeatedly used for the extraction of acetic acid and the back-extraction of acetic acid by NaOH. The amount of acetic acid extracted in the microcapsules was plotted against the number of times the microcapsules had been reused as shown in Fig. 11. The amounts of acetic acid extracted each time were almost the same as that for the first time. This shows the extraction capacity of the microcapsules is constant in repeated use and the leakage of TOA from the microcapsules during the extraction process is negligible. The large size microcapsules prepared at 30 wt% TOA and 20 wt% toluene were strong enough for repeated use. However, the durability of the microcapsules prepared at higher concentrations of TOA and toluene decreased with their increasing concentration.

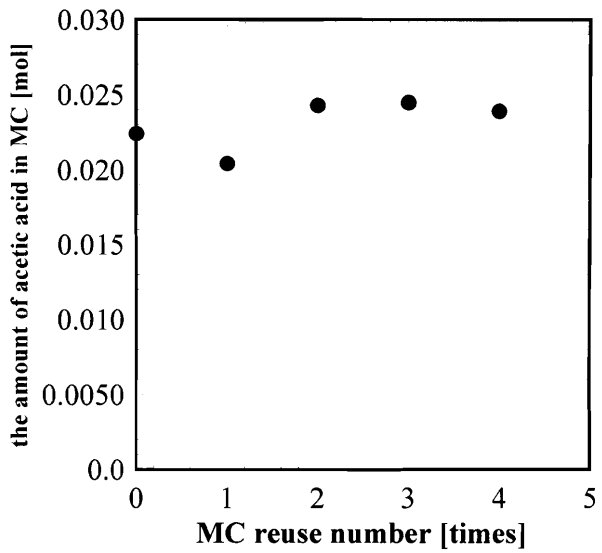


Fig. 11 Relationship between the amounts of acetic acid extracted in the microcapsules prepared at 30 wt% TOA and 20 wt% toluene and the reuse times. Styrene:DVB = 1:1.

4. Conclusion

Large millimeter size microcapsules containing TOA were successfully prepared by *in situ* polymerization with a gel inclusion of an organic droplet. The structure of the microcapsules changed with the preparation conditions such as the TOA and toluene concentrations in the organic phase. When the TOA and toluene concentrations were high, the strength of the microcapsules became weak and serious leakage of TOA was observed. The extraction of acetic acid by the microcapsules was successfully achieved and the extraction rate was relatively fast in spite of the large size of the microcapsules. TOA entrapped in the microcapsules showed the same extraction properties as that of the solvent extraction system. The microcapsules could be used several times over without a decrease in the extraction capacity.

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