The effect of the structure of each component on the o/w microemulsion droplet size and stability

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Abstract

The oil in water type ME of 4 component system was composed with POE monoalkyl ether and POE sorbitan monoalkyl ester as surfactant, saturated hydrocarbon, side chain structure and aromatic structure as oil, and glycerine as cosurfactant using high pressure homogenizer. The objective of this study was to examine the role of surfactant and oil structure on droplet size and stability. The experimental results showed that the droplet size was smaller with bigger polarity of oil, less hydrocarbon, longer hydrophilic chain of surfactant and higher concentration of glycerine. SQ and LP systems showd very stable but AB and ISB system unstable microemulsion.

Introduction

Microemulsion (ME) is called swollen micelle solution or transparent emulsion[1~5]. Generally, in three components system, the ME contains water, oil and surfactant. When the ME contains cosurfactant, it is called four components system[6~7]. The droplet size of dispersed phase is 10 to 100 nm in ME[8~9]. Because of very small droplet size, the ME is optically isotropic, is transparent, has high fluidity and can contain more oils than that in solubilized micelle[10~14]. In microscopic point of view, ME is transparent and is thermodynamically stable single phase. In the macroscopic point of view, even if the ME is transparent or semi- transparent and thermodynamically unstable two phase, the ME is defined as stable dispersed phase within limited time period[15~17]. The ME is applied in many different industrial field such as fuel, cosmetics, pharmaceutical, food, protein separation or tertiary oil recovery[18~24]. Therefore, many researchers are focusing on the studying of ME.

In the classical ME research, anionic surfactant and medium chain length alcohol, which can cause skin irritation problem were generally used, so it was very difficult to apply these techniques in cosmetic or pharmaceutical field. Because of this problem, the attention is getting commercially increased using nonionic surfactant which has less skin irritation is being used with glycerine which is commonly used for moisturizer as cosurfactant, which is stable dispersed phase within limited time period.

Using high pressure homogenizer, which is operated at maximum 23,000 psi can reduce the surfactant usage by size reduction in accordance with cavitation, impaction and shear force. The high pressure homogenizer can produce narrow range of droplet size and create ultra fine emulsion like less than 0.5 μm[25].

Materials and Methods

Materials

Oil in water ME was made with POE(12) lauryl ether (LE), POE(15) cetyl ether (CE), POE(15) stearyl ether (SE), POE(20) sorbitan monolaurate(SL), POE(20) sorbitan monopalmitate(SP) and POE(20) sorbitan monostearate(SS) as surfactant, squalane(SQ), liquid paraffin (LP), octyl stearate(OS), octyl palmitate(OP), alkyl benzoate(AB) and isostearyl benzoate(ISB) as oil, and glycerine(Gly) as cosurfactant.

Tables 1 to 2 are shown the summary of the materials.

Methods

ME preparation

Based on the previous experiments[26] , 5% of oil, 10% of surfactant, x% of Gly and (85-x)% of water was used. After each sample was mixed at 70±1°C and past through the Microfluidizer (Model 110Y, Microfluidics, U.S.A.) of which high pressure homogenizer. And the sample was cooled down to ambient temperature. The operating condition was 10,000 psi and 5 passes.

Particle size measurements

The obtained samples were stored for four weeks at room temperature and measured five times at right angle. The data was obtained with average value of five measurements. The measuring equipment was laser light scattering system (PCS 4700, Malvern Co., UK).

Results and Discussions

The effect of structure of oil in ME droplet size

The order of droplet size is SQ & LP> OS & OP> AB & ISB as shown in Figures 1 and 2. The droplet size of non-polar oil system was bigger than that of polar oil system. Because the non-polar oil has probably more affinity with hydrophobic part of micelle, the oil was dissolved in core of micelle, semi-polar oil was dissolved within palisade, and polar oil was dissolved in mantle due to higher hydrophilic affinity with water than that of semi-polar.

Therefore, the dissolving space can be ordered as mantle> palisade> core. It was observed that the bigger dissolving space is the smaller droplet size. The droplet size was decreased with increasing polarity due to increasing quantity of solubilization. The droplet size was increased with increasing the main chain length of hydrophobic part in oil.

The effect of structure of surfactant on droplet size of ME

The droplet size of POE monoalkyl ether type surfactant such as LE, CE, SE was compared to that of POE sorbitan monoalkyl ester type surfactant such as SL, SP, SS in microemulsion (ME). The droplet size was observed in the following order; LE> CE> SE and SL> SP> SS. This phenomena could be identified by comparing carbon length in hydrophobic alkyl chain of surfantant with droplet size; ether type SE which has 18 of carbon was compared to ester type LE which has 12 of carbon. The SE has more carbon and smaller droplet size than LE. The same phenomena was observed for SS to SL. Because the longer the hydrophobic carbon in surfactant the more chance to meet micelle this can increase the solubility of oil. The droplet size is getting smaller due to the high solubility of oil. For polar oil, the droplet size is even smaller than that in non-polar oil because of higher solubility. It can be concluded that the droplet size is getting smaller because the longer carbon chain of surfantant can increase the solubility.

The effect of quantity of glycerine, polarity of oil and HLB of surfactant in stability of ME

Figures 3 to 8 showed the system of POE stearyl ether/glycerine/water/oil. SQ, LP, OS, OP, AB and ISB were used for Figure 3 to 8, respectively. These graphs showed the droplet size changed in time. The droplet size was decreased with increasing the quantity of glycerine in the system. The growing ratio of droplet size with time was observed in the order of SQ <LP <OS <OP <AB <ISB system. The SQ and LP systems showed very stable microemulsion but AB and ISB showed unstable microemulsions. Also, the growing ratio was increased with more quantity of glycerine. The phenomena of smaller particle size with increasing concentration of glycerine can be explained with that OH radical of glycerine can widen the head area of hydrophilic group of micelle, so solubility can be increased due to easy oil penetration.

The reason of stable ME for SQ and LP can be explained with that non-polar oil is placed inside of core rather than placed outside, thus it is very stable. On the other hands, polar oil is placed in mentle which can be effected easily by glycerine. Therefore, with increasing glycerine concentration, the droplet size can be increased by coalescence which can be occurred by widening head area of hydrophilic group of surfactant and movement of non-polar oil molecule in mentle.

Figures 9 to 14 showed the system of POE sorbitan stearate/glycerine /water/oil. SQ, LP, OS, OP, AB and ISB were used for Figures 9 to 14, respectively. These graphs showed the droplet size change with time and concentration of glycerine. These graphs showed very similar trend those obtained in Figures 3 to 8. However, it was observed that the growing ratio of droplet size is slightly bigger than that of stearyl ether. These can be explained by difference between HLB of surfactant to required HLB(HLB_{req}) HLBreq of oil is 9.5 to 13 (SQ=9.5; LP=10.5; OS=11.4; OP=11.5; AB=12 and ISB=13). HLB of stearyl ether is 12 and of stearate is 14.9. It can be concluded that the difference between HLB to HLB_{req} for SS is bigger than that of SE, thus the growing ratio of droplet size is bigger.

Conclusion

The droplet size was smaller with bigger polarity of oil, less hydrocarbon of oil, longer hydrophilic chain of oil and higher concentration of glycerine. Non-polar oil placed in core was much more stable compare to placed in mantle or palisade. The SQ and LP systems showed very stable but AB and ISB systems unstable microemulsion. The droplet size was smaller when there is less difference between HLB to required HLB.

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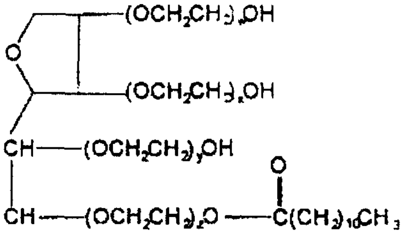
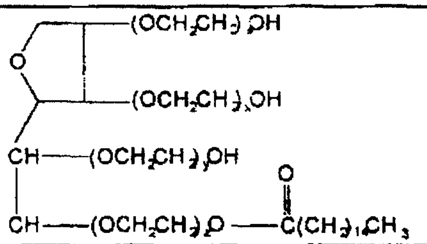
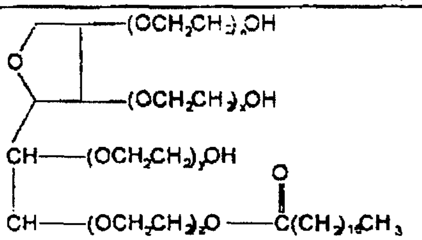
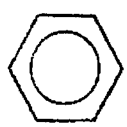
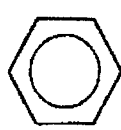
Table 1. The chemical formula of surfactants

Surfactant	Chemical formula	H L B	Maker
POE(12) lauryl ether (LE)	$C_{12}H_{25}OCH_2CH_2(OCH_2CH_2)_{11}OH$	13	Nihon emulsion Co. , Ltd.
POE(15) cetylether (CE)	$C_{16}H_{33}OCH_2CH_2(OCH_2CH_2)_{14}OH$	13	Nihon emulsion Co. , Ltd.
POE(15) stearyl ether (SE)	$C_{18}H_{37}OCH_2CH_2(OCH_2CH_2)_{14}OH$	12	Nihon emulsion Co. , Ltd.
POE(20) sorbitan monolaurate (SL)		16.7	ICI Americas Inc. U.S.A
POE(20) sorbitan monopamitate (SP)		15.6	ICI Americas Inc. U.S.A
POE(20) sorbitan monostearate (SS)		14.9	ICI Americas Inc. U.S.A

(W+X+Y+Z=20)

Table 2. The chemical formula of oils

Oil	Chemical formula	HLB_{req}	Maker
Squalane (SQ)	CH_3 H_3C / H_3C $CHCH_2(CHC_3H_6)_2CH_2$	9.5	Nippon Petro. Chem. Co. Japan
Liquid paraffin (LP)	$CH_3(CH_2)_{18\text{-}20}CH_3$	10.5	Dow Corning U.S.A
Octyl stearate (OS)	$CH_3(CH_2)_{16}C(=O)-OCH_2CH(CH_2)_3CH_3$ with CH_2CH_3 on CH	11.4	Unichema U.S.A
Octyl palmitate (OP)	$CH_3(CH_2)_{14}C(=O)-OCH_2CH(CH_2)_3CH_3$ with CH_2CH_3 on CH	11.5	Unichema U.S.A
Alkyl benzoate (AB)	 — $COO\,CH_2C_nH_{2n+2}$ (n = 11-14)	12	Fintex U.S.A
Isostearyl benzoate (ISB)	 — $COO\,C_{18}H_{37}$	13	Fintex U.S.A

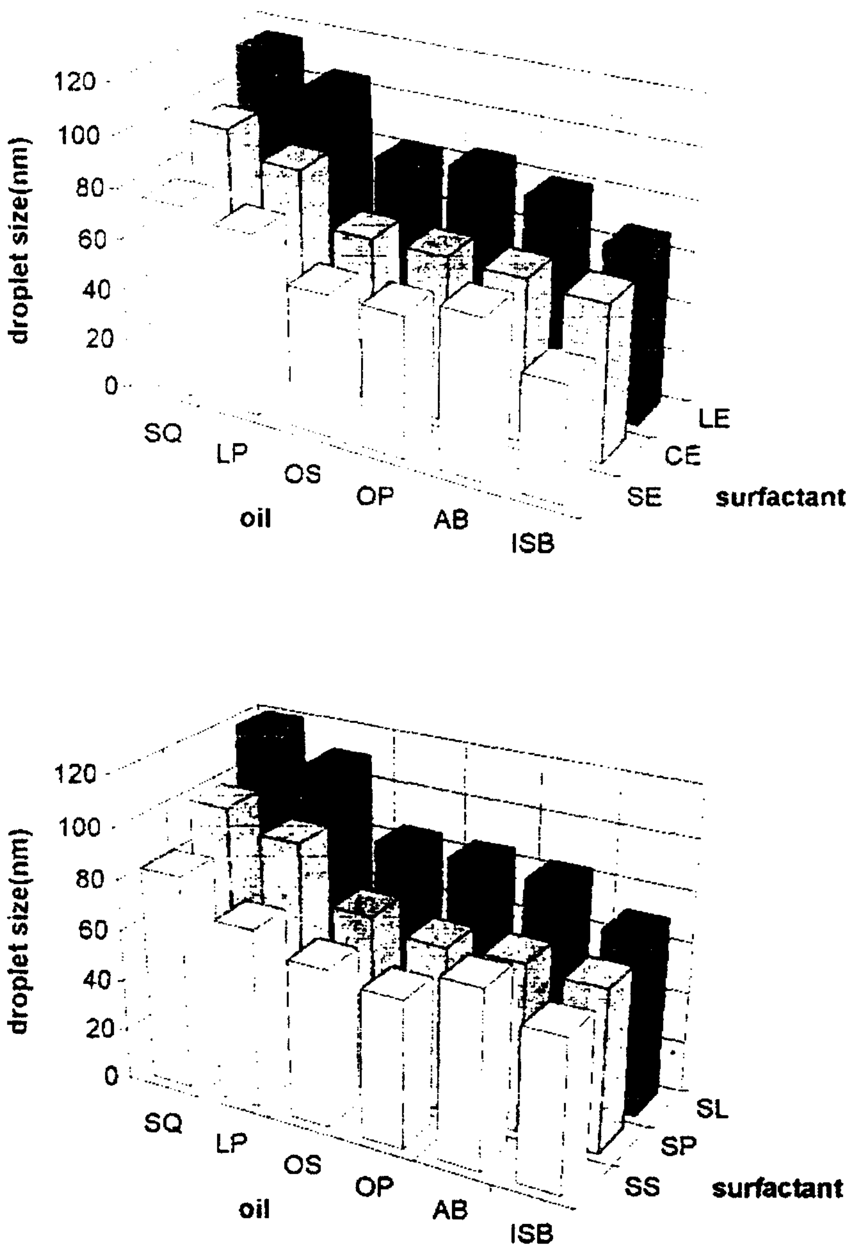


Fig. 1. The effect of the various surfactants and oils on droplet size.

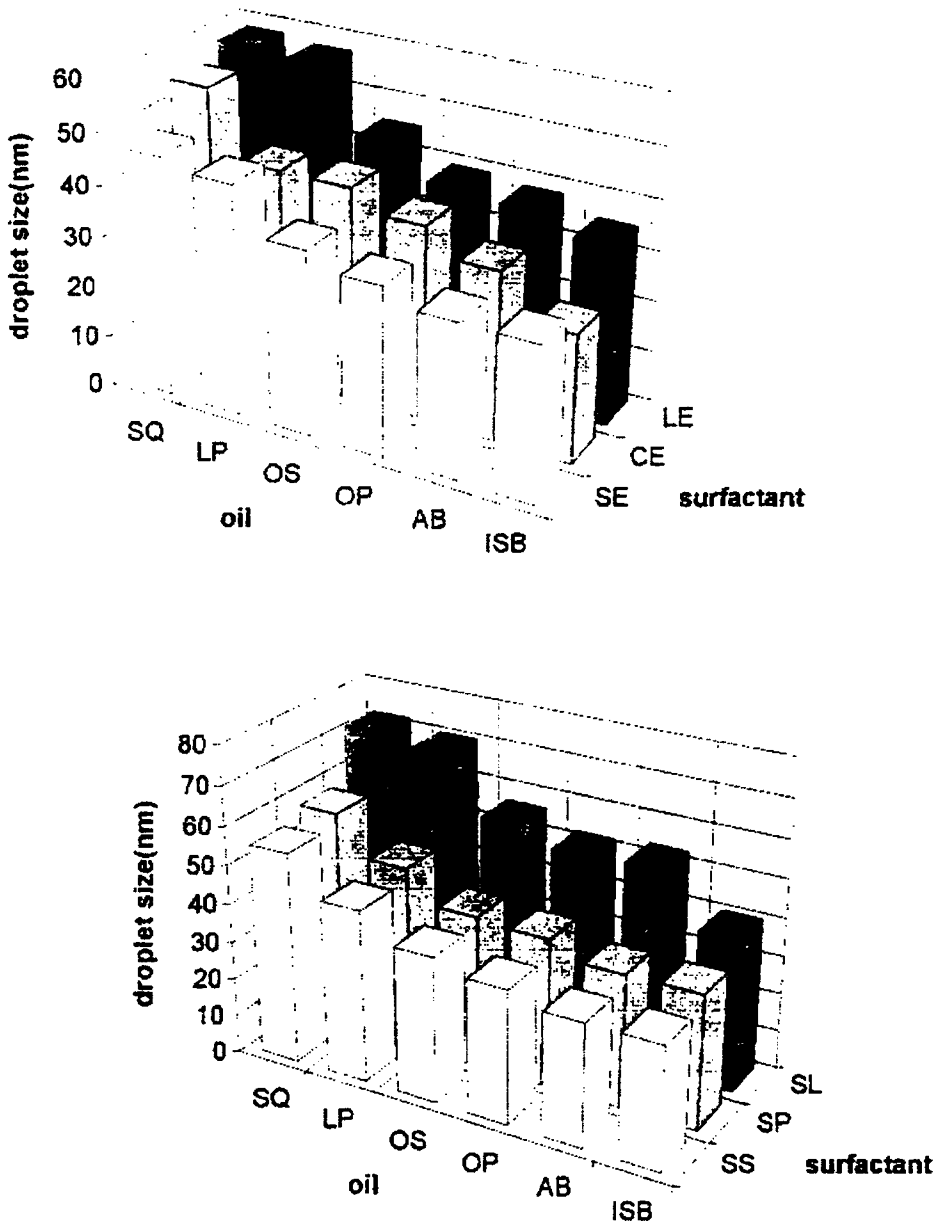


Fig. 2. The effect of the various surfactants and oils on droplet size.(Gly20%)

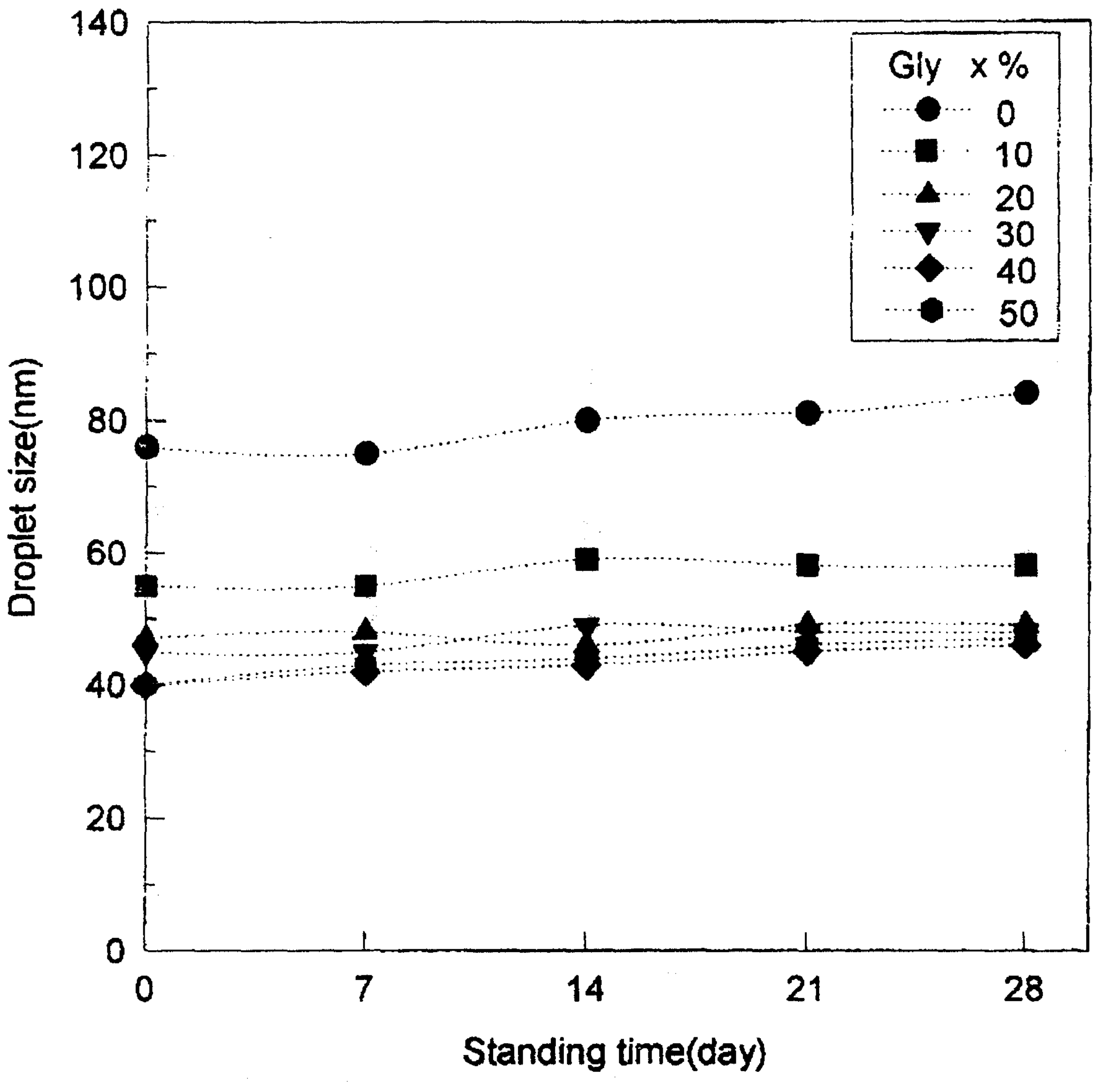


Fig. 3. Microemulsion droplet size vs. standing time.

(SE(10%) / SQ(5%) / Gly(x%))

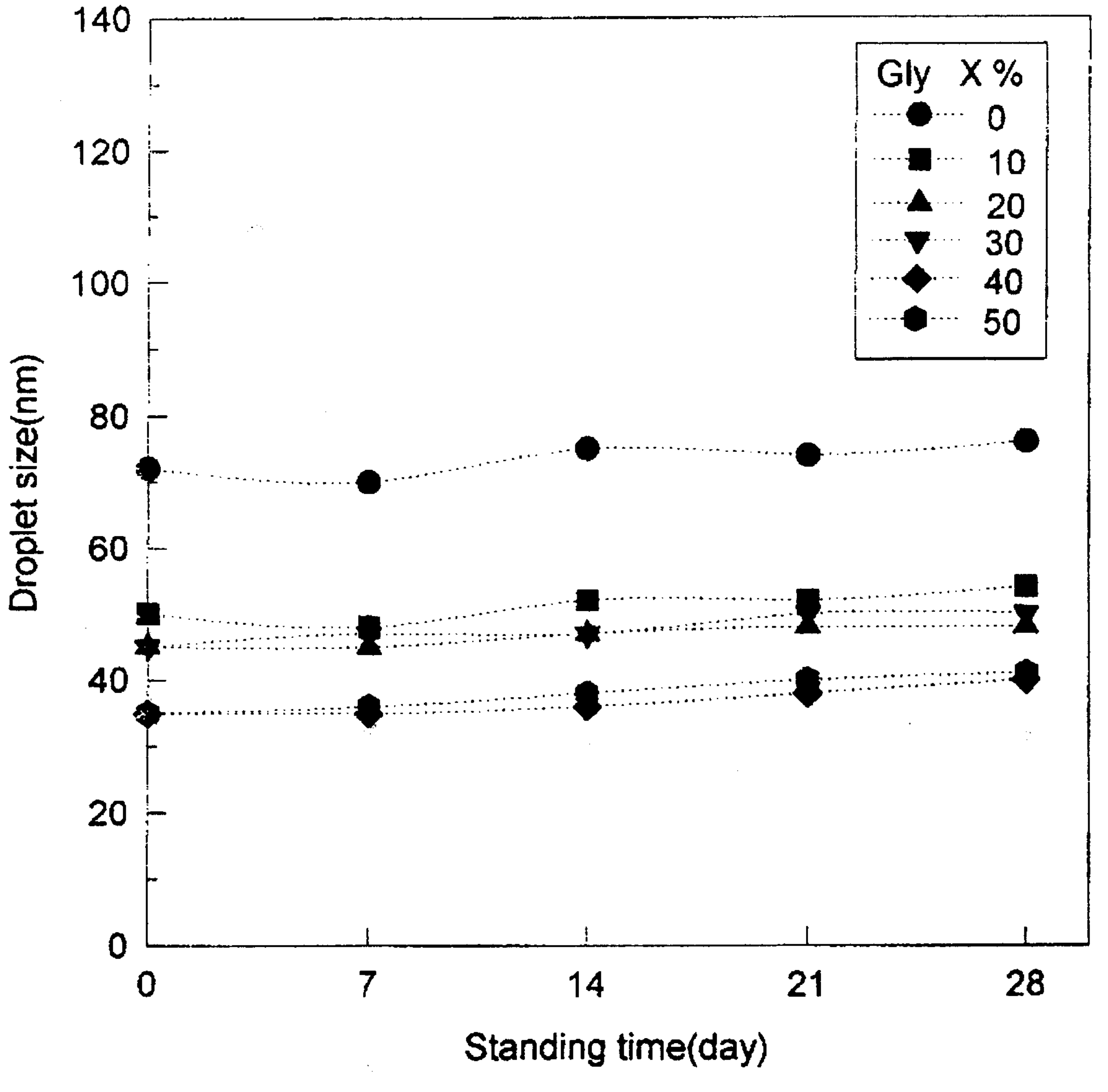


Fig. 4. Microemulsion droplet size vs. standing time.
(SE(10%) / LP(5%) / Gly(x%))

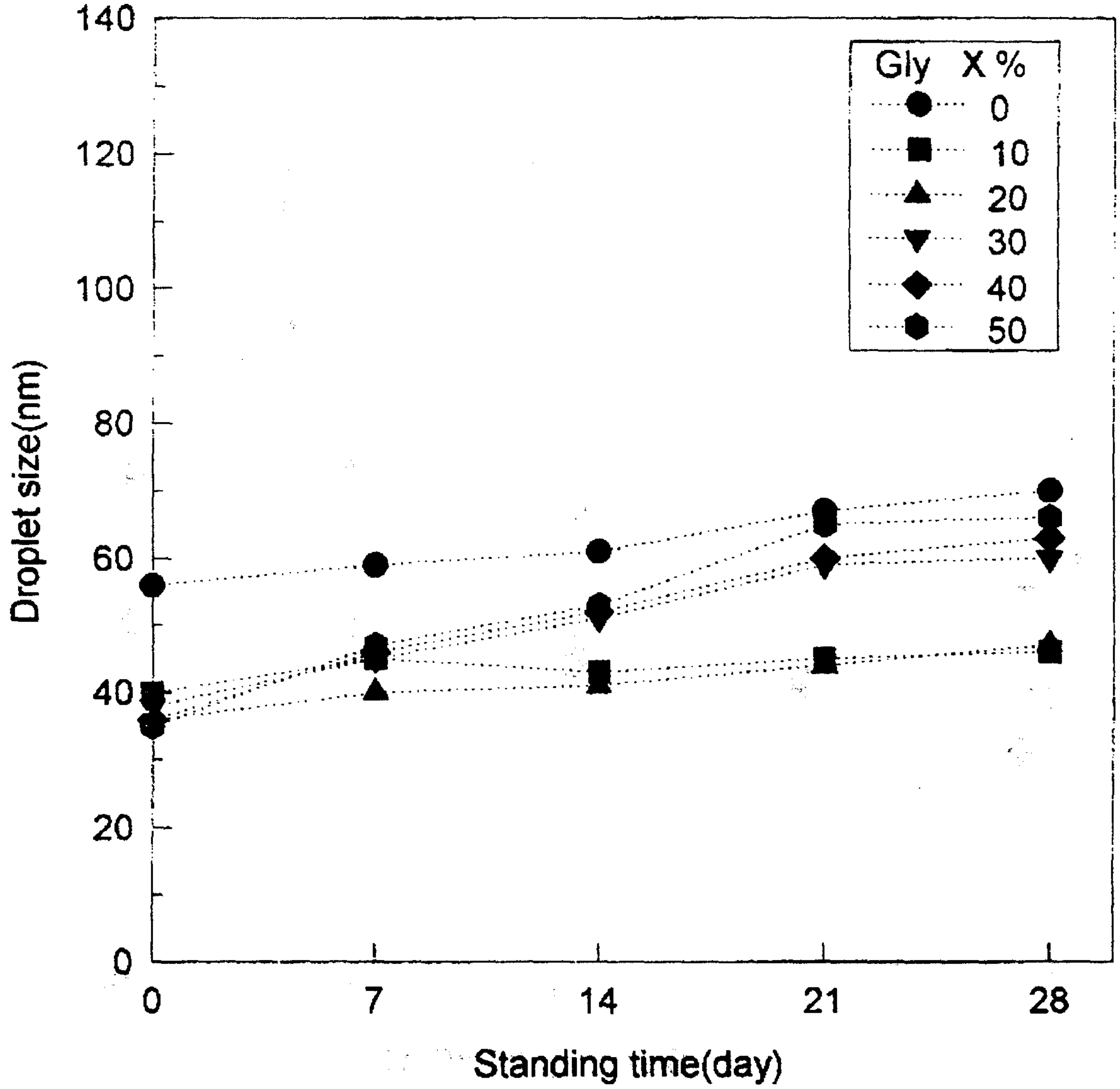


Fig. 5. Microemulsion droplet size vs. standing time.

(SE (10%) / OS(5%) / Gly(x%))

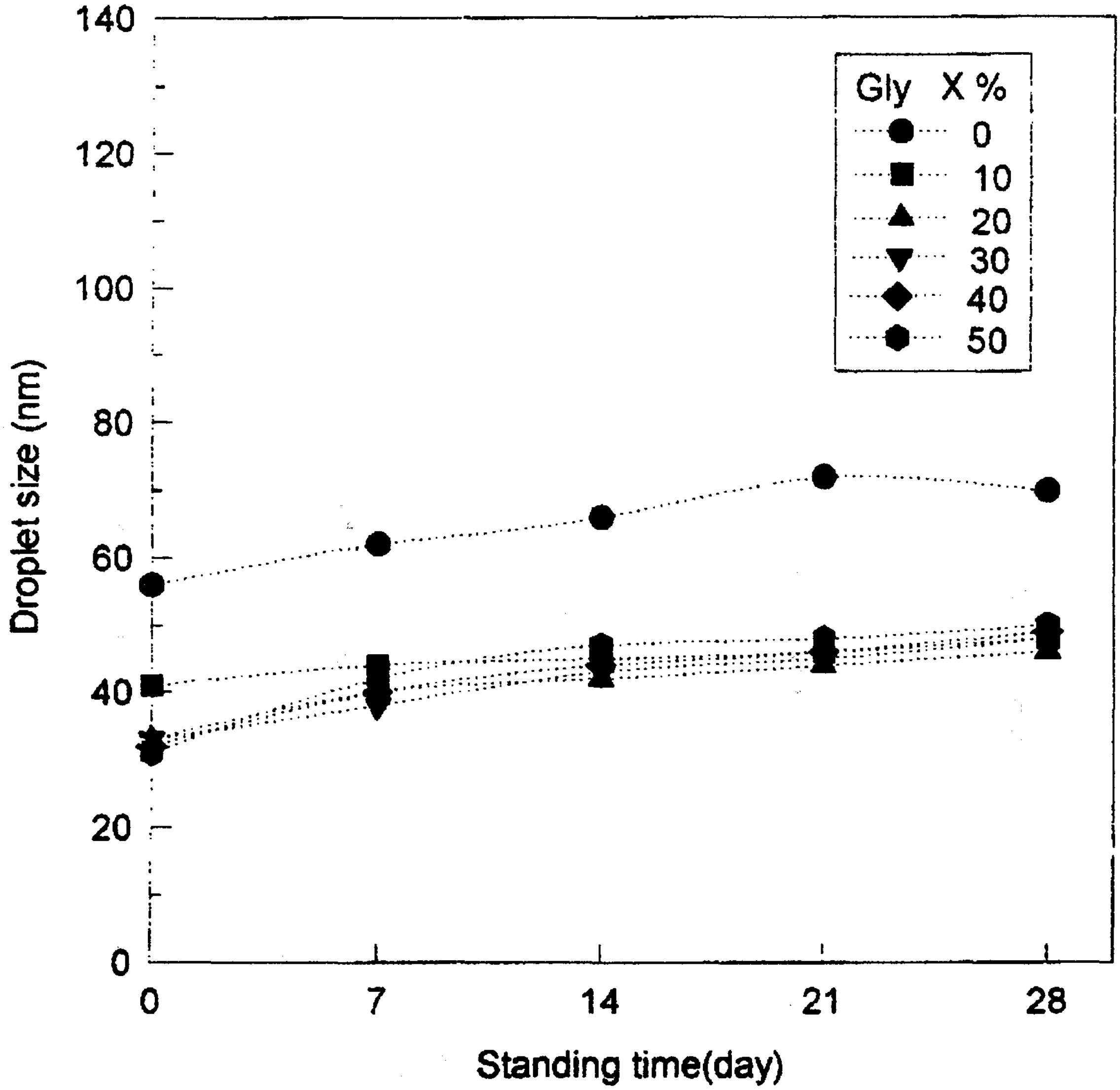


Fig. 6. Microemulsion droplet size vs. standing time.

(SE(10%) / OP(5%) / Gly(x%))

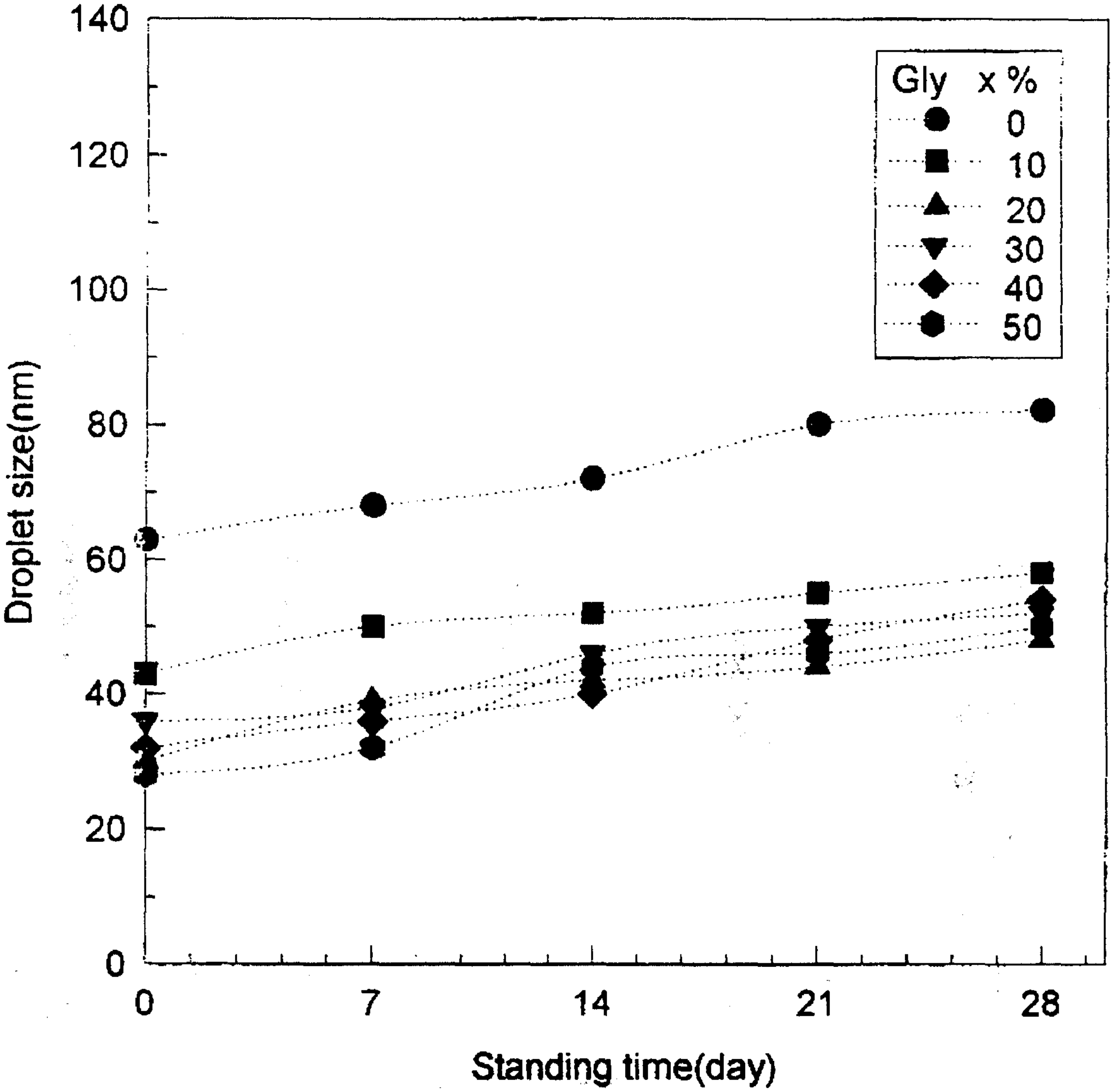


Fig. 7. Microemulsion droplet size vs. standing time.

(SE(10%) / AB(5%) /Gly(x%))

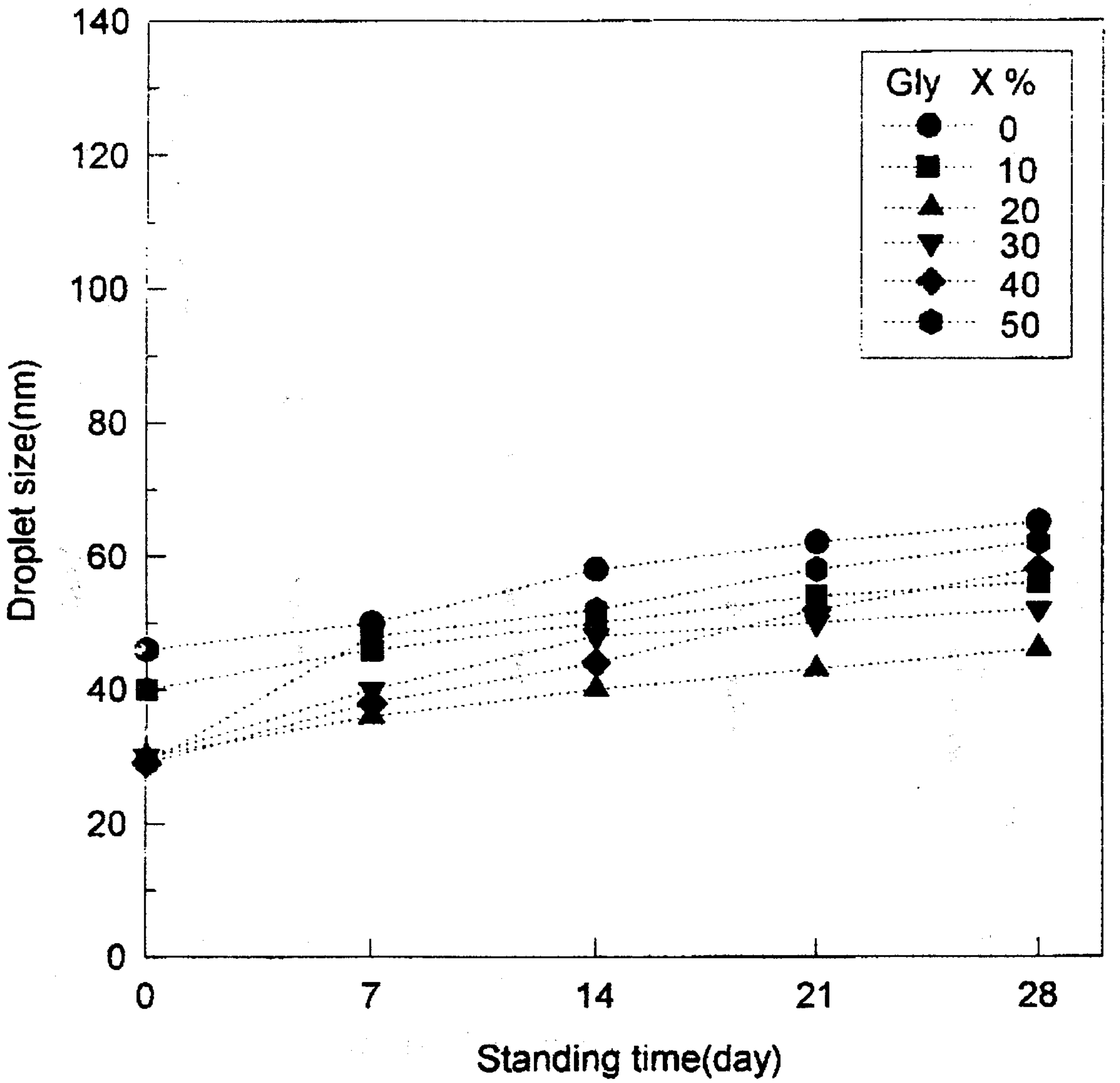


Fig. 8. Microemulsion droplet size vs. standing time.

(SE(10%) / ISB(5%) / Gly(x%))

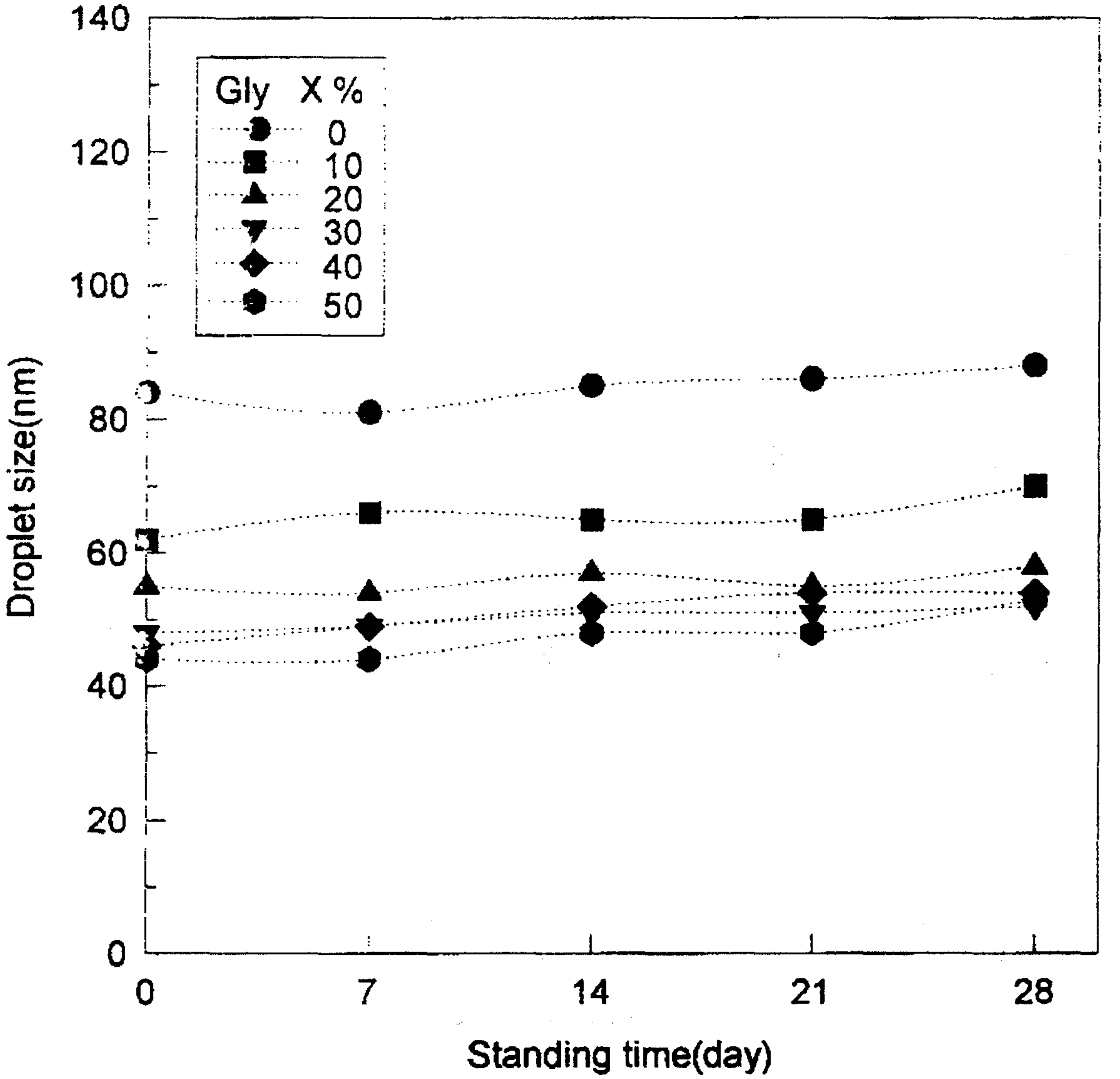


Fig. 9. Microemulsion droplet size vs. standing time.

(SS(10%) / SQ(5%) / Gly(x%))

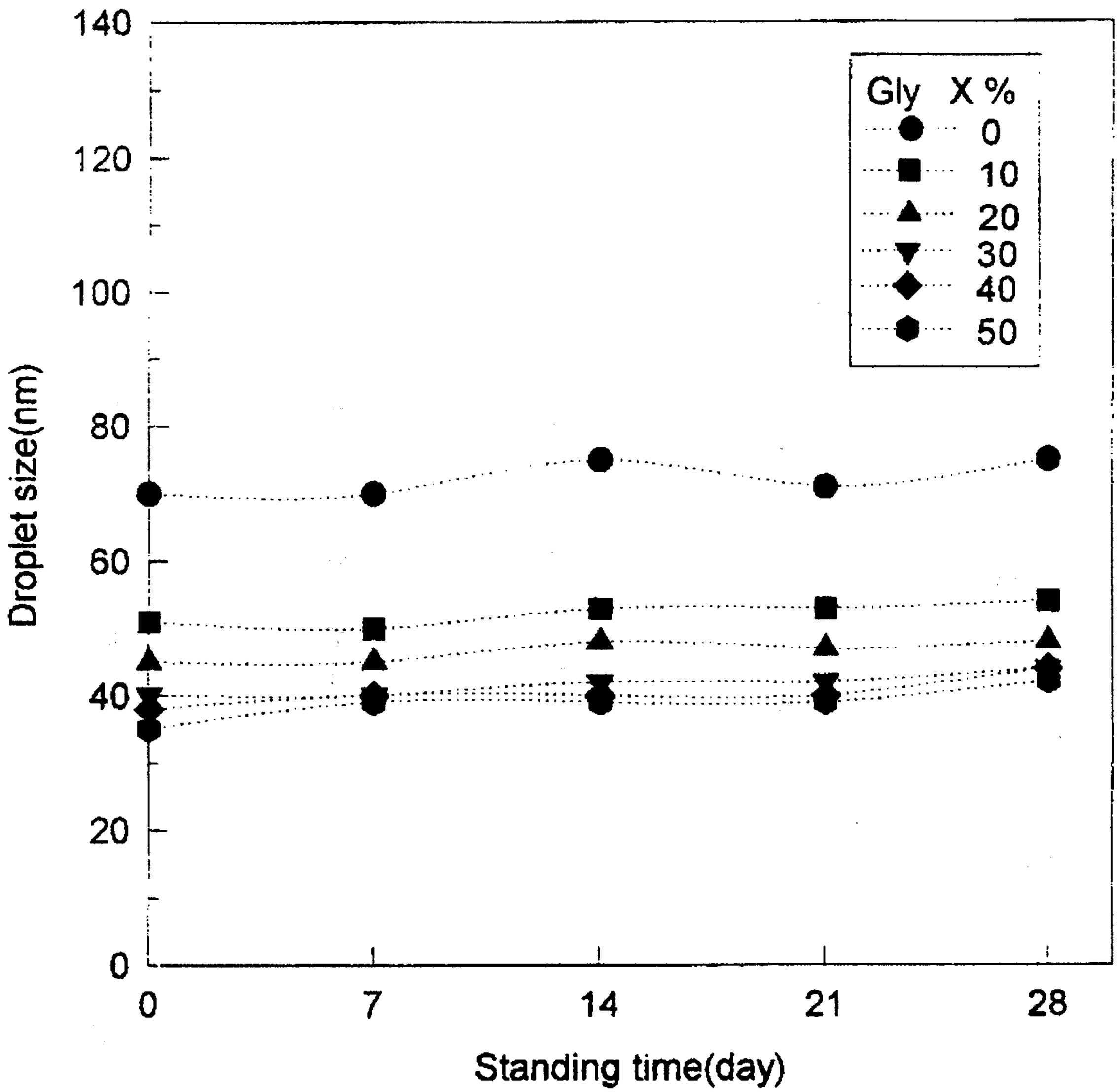


Fig. 10. Microemulsion droplet size vs. standing time.

(SS(10%) / LP(5%) / Gly(x%))

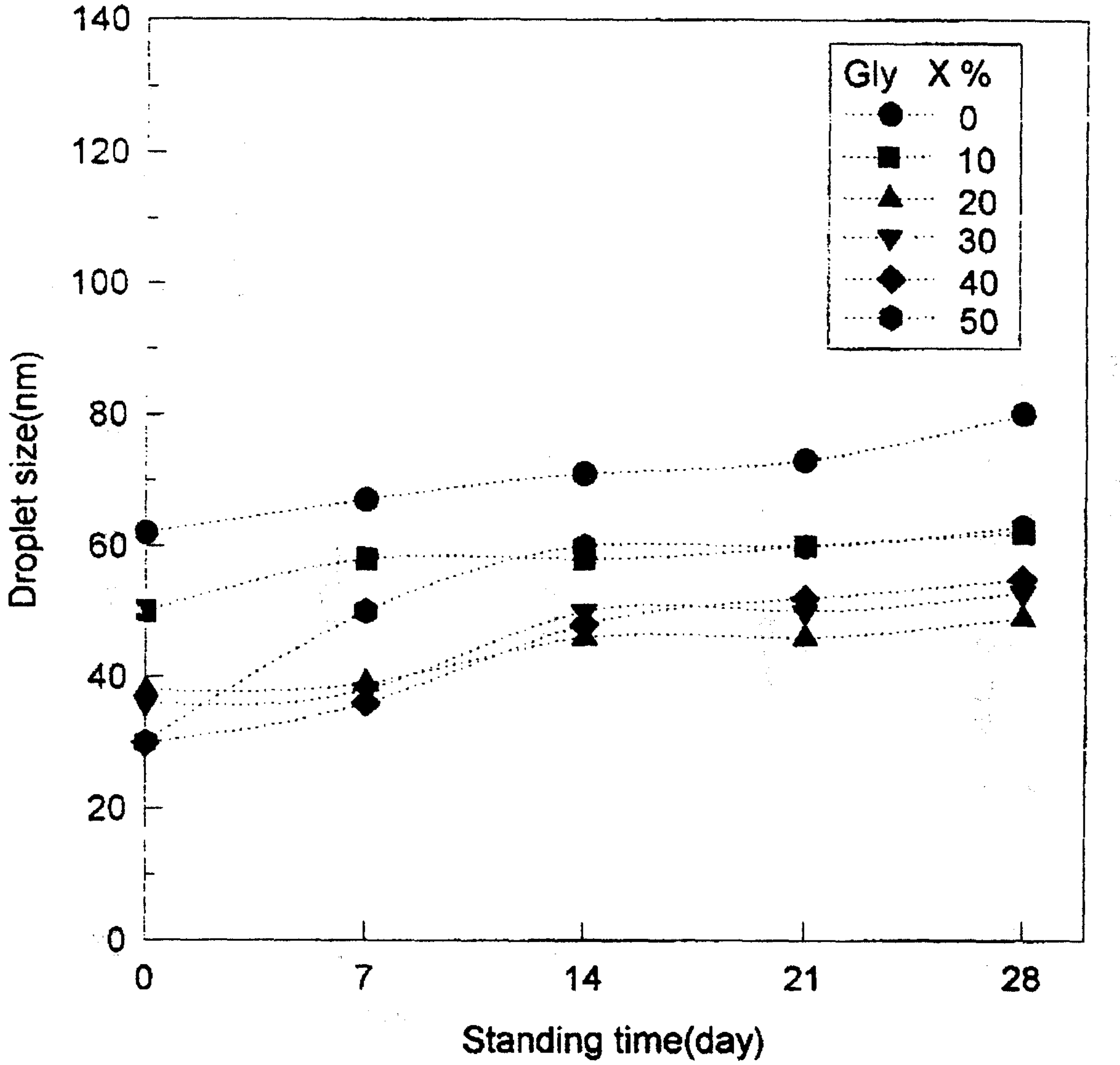


Fig. 11. Microemulsion droplet size vs. standing time.

(SS(10%) / OS(5%) / Gly(x%))

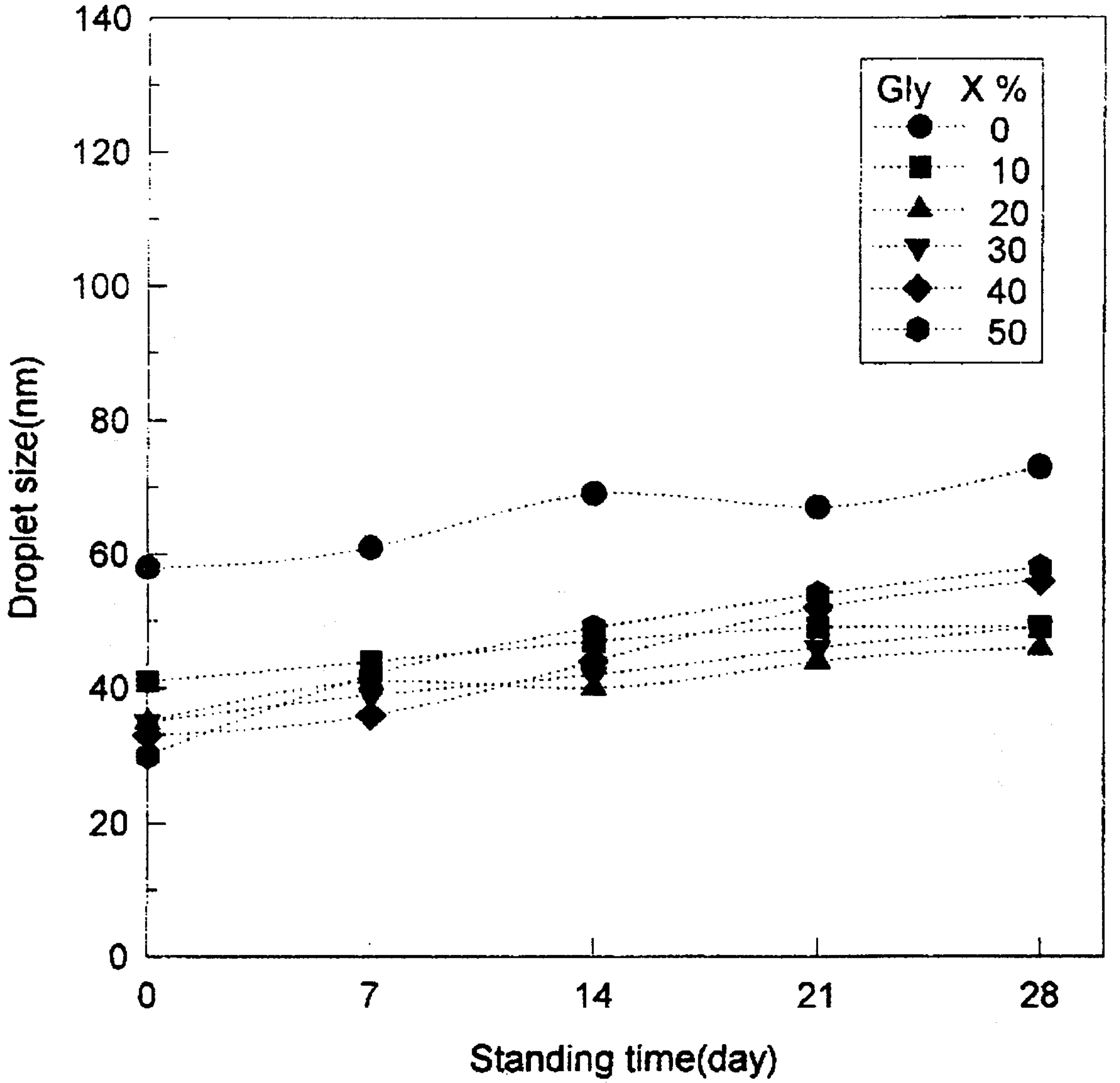


Fig. 12. Microemulsion droplet size vs. standing time.

(SS(10%) / OP(5%) / Gly(x%))

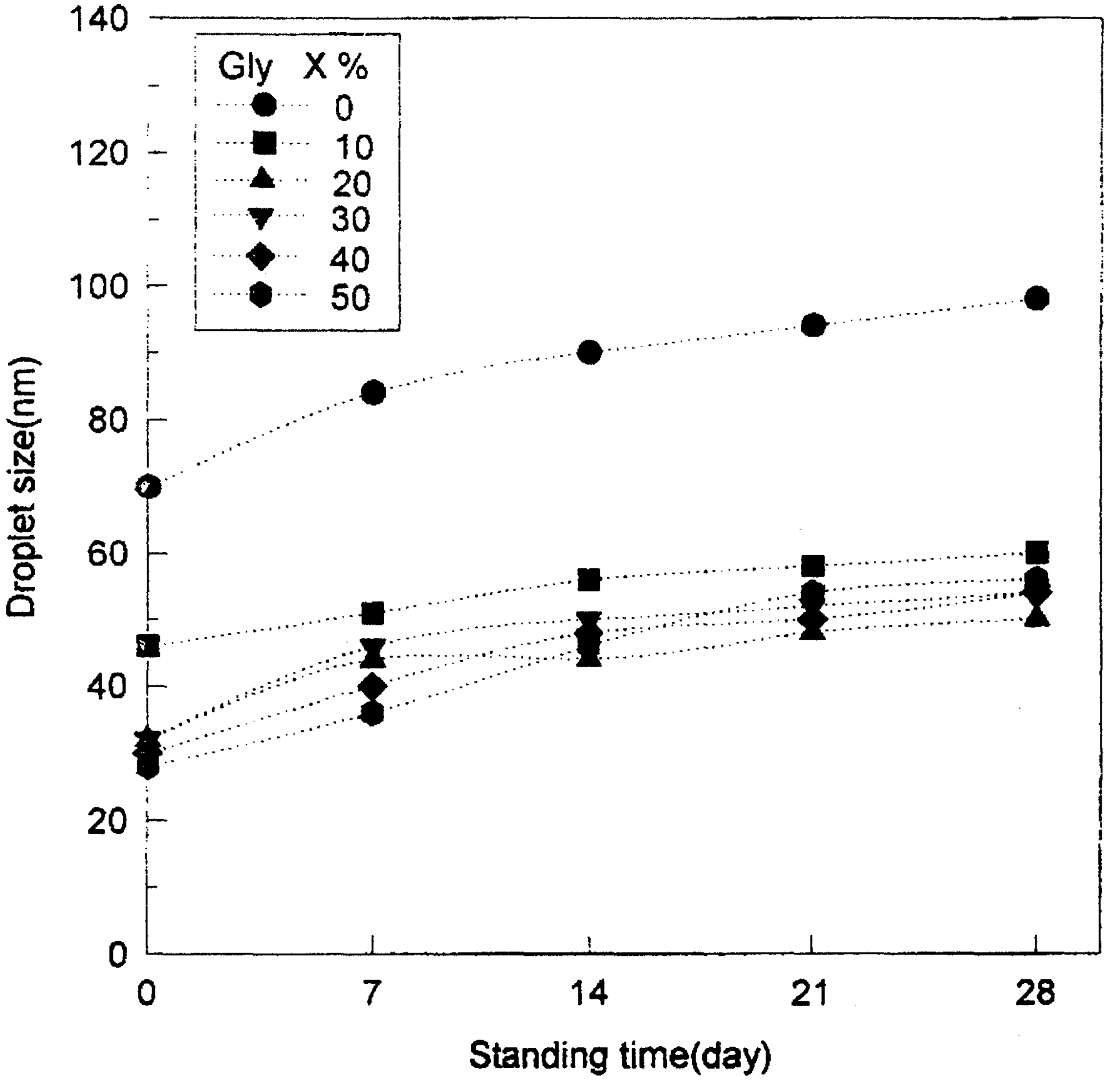


Fig. 13. Microemulsion droplet size vs. standing time.

(SS(10%) / AB(5%) / Gly(x%))

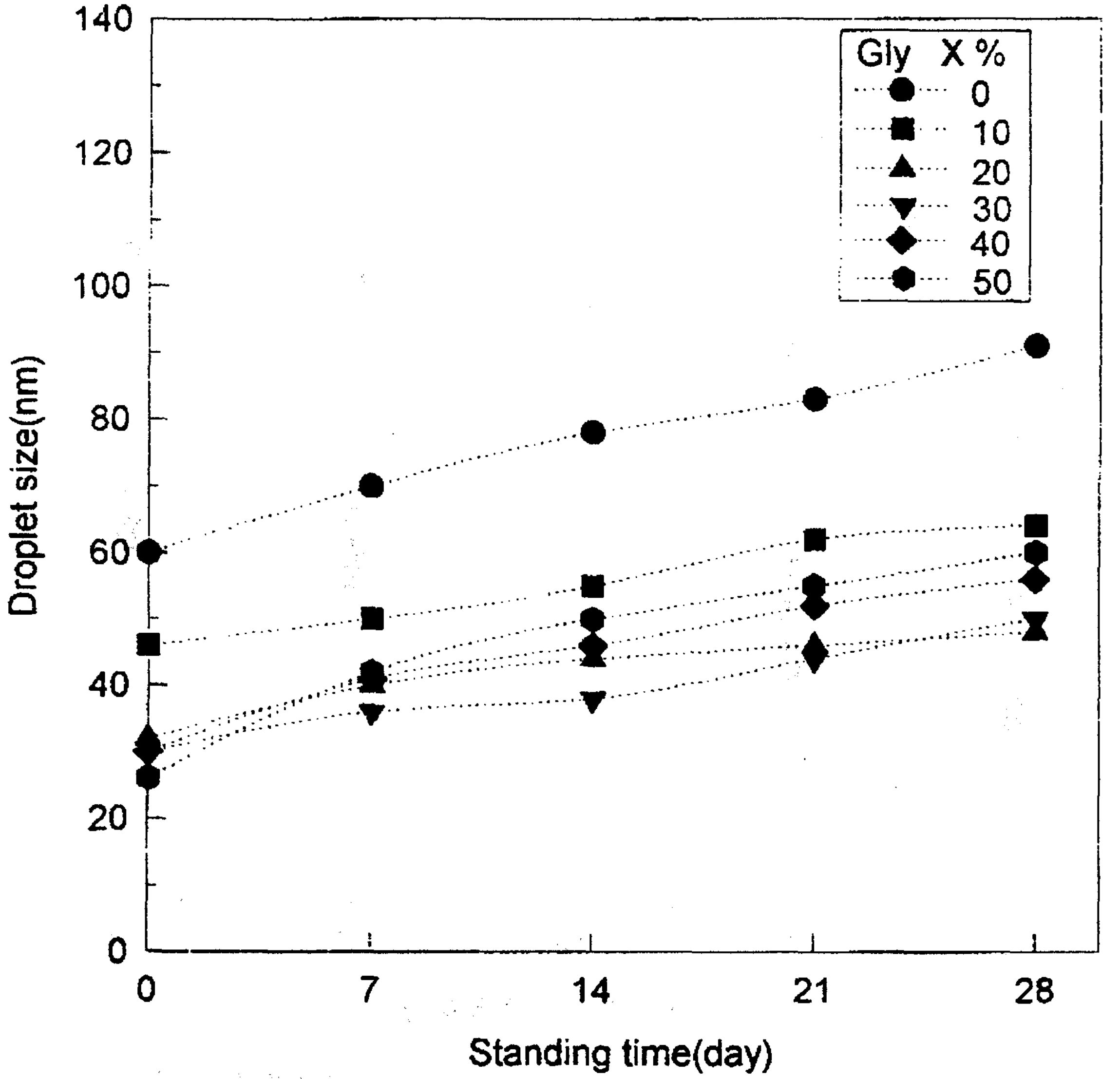


Fig. 14. Microemulsion droplet size vs. standing time.

(SS(10%) / ISB(5%) / Gly(x%))