Original Article

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Preparation and physicochemical properties of surfactant-free emulsions using electrolytic-reduction ion water containing lithium magnesium sodium silicate

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ABSTRACT: Surfactant-free emulsions by adding jojoba oil, squalane, olive oil, or glyceryl trioctanoate (medium chain fatty acid triglycerides, MCT) to electrolytic-reduction ion water containing lithium magnesium sodium silicate (GE-100) were prepared, and their physiochemical properties (thixotropy, zeta potential, and mean particle diameter) were evaluated. At an oil concentration of 10%, the zeta potential was –22.3 – –26.8 mV, showing no marked differences among the emulsions of various types of oil, but the mean particle diameters in the olive oil emulsion (327 nm) and MCT emulsion (295 nm) were smaller than those in the other oil emulsions (452-471 nm). In addition, measurement of the hysteresis loop area of each type of emulsion revealed extremely high thixotropy of the emulsion containing MCT at a low concentration and the olive emulsion. Based on these results, since surfactants and antiseptic agents markedly damage sensitive skin tissue such as that with atopic dermatitis, surfactant- and antiseptic-free emulsions are expected to be new bases for drugs for external use.

Keywords: Surfactant-free emulsions, electrolytic-reduction ion water, lithium magnesium sodium silicate, thixotropy, rheology

1. Introduction

Magnesium aluminum silicate is a laminar clay material and saponite that belongs to the smectite group, markedly increases viscosity, and shows high thixotropy when dispersed in various solvents (*1*). Using these properties, smectite such as magnesium aluminum silicate or lithium magnesium sodium silicate is widely used as a texture enhancer in cosmetics, color antisettling agent in paints, catalyst in specific reactions, adsorbent in functional films, and an anti-dripping agent in adhesives (*2*).

Electrolytic-reduction ion water (ERI) is ion water with physically excess electrons that is obtained by electrolysis of natural water using a special diaphragm system. Due to its special alkalinity and negatively charged ions, ERI removes dirt and bacteria as sources of odor by its detachment action, and, therefore, has cleansing, deodorizing, bactericidal, and anti-dust effects (*3,4*). Unlike synthetic surfactants, ERI does not burden the environment, and, therefore, is mainly used as a cleansing agent for various industrial products.

We previously prepared magnesium aluminum silicate solutions using various solvents including ERI, and reported their rheology characteristics by measuring oscillation employing a stress control-type rheometer (*5*). Using ERI as a dispersion medium, conversion from gel to sol occurred at a low frequency (external factor). In addition, gel was prepared using ERI containing magnesium aluminum silicate as smectite, and gel characteristics for various types of salt were evaluated in detail (*6*). As a result, the presence of Ca^{2+} made the system unstable, but uni- and multi-valent cations excluding Ca^{2+} markedly improved gel stability.

On the other hand, emulsions for medicine such as creams are generally prepared with lecithin as an amphoteric surfactant or polysorbate as a nonionic surfactant. Some surfactants excluding lecithin are known to induce stimulant dermatitis, and may sometimes cause allergic symptoms (*7*). Considering biological safety, surfactant-free emulsions are optimal. However, without using surfactants, emulsification itself is difficult, and temporal stability is poor. Therefore, using the cleansing effects of ERI, surfactant-free stable emulsions were prepared, and their functionality was reported (*8*). Surfactant-free emulsions prepared with ERI were more stable and showed a smaller mean diameter than those containing egg yolk lecithin as a surfactant. These results suggested that skin-irritating reactions and allergic symptoms due to surfactants can be reduced by preparing

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surfactant-free stable emulsions using the emulsification effect of ERI. Therefore, we prepared smectite gel using ERI as a dispersion medium, and reported its physiochemical characteristics (*5,6*).

In addition, to evaluate application to medical drugs, we evaluated the healing-promoting effects of ERI on burns and atopic dermatitis, and observed its effectiveness and alleviation of these symptoms (*9-12*).

Based on the above reports, ERI compared with purified water can allow the preparation of drugs with a drug delivery system (DDS) that can maintain the gel state. ERI with emulsification characteristics and a gelling drug maintaining function are useful for preparing controlled-release transdermal therapeutic drugs.

In this study, we prepared surfactant-free emulsions by adding various types of oil to ERI containing lithium magnesium sodium silicate as smectite, and evaluated their physiochemical characteristics.

2. Materials and Methods

2.1. *Materials*

ERI containing lithium magnesium sodium silicate (*13*) (GE-100: A. I. System Product Corp., Aichi, Japan), jojoba oil (Wako Pure Chemical Industries, Ltd., Osaka, Japan), squalane and olive oil (Kanto Chemical Co., Inc., Tokyo, Japan), were used as purchased and glyceryl trioctanoate (medium chain fatty acid triglycerides, MCT, Panacet® 800 were kindly provided by NOF Corporation (Tokyo, Japan). All the other reagents were of analytical grade.

2.2. *Preparation of surfactant-free emulsions*

ERI containing 3% lithium magnesium sodium silicate (GE-100) was mixed with 0.1, 1, and 10% oil (jojoba oil, squalane, olive oil, or MCT), and samples of various emulsions (100 g) were prepared using an ultrasonic homogenizer (UH-300: SMT Co., Ltd., Tokyo, Japan) under the following emulsification conditions: standard horn, 12 ø; frequency, 20 kHz; processing time, 5 min, continuously.

2.3. *Zeta potential and particle size measurement*

The zeta potential and mean particle diameter of oil droplets in each sample were measured using a zeta potential analyzer (ZEECOM ZC-3000M, Microtec Co., Ltd., Chiba, Japan). Palladium was used as the electrode material of the measurement cell, and a special quartz cell (width, 10 mm) fixed with a Teflon block with a distance between positively biased electrodes of 64 mm and a distance between reference electrodes of 36 mm was used. Data analysis was performed using personal computer measurement system software for ZEECOM ZC-3000. For the measurement of the zeta potential, oil droplet particles electrophoresed after voltage application to the positively biased electrode so that 10.0 V could be applied to the reference electrode were automatically tracked, and the zeta potential was calculated from their electrophoretic mobility using the Smoluchowski equation. For the measurement of the mean particle diameter of oil droplets, the cell containing a sample was irradiated with a laser, and the Brownian motion of particles was measured per unit of time without voltage application, and the particle diameter was calculated using the Stokes-Einstein equation..

2.4. *Rheology measurement*

For rheology measurement, a shear rete-shear stress-controlled rheometer RC20 (RheoTec Messtechnik GmbH, Ottendorf-Okrilla, Germany) as a single cylindrical rotational viscometer (Brookfield type viscometer) was used (*14,15*). Assuming room temperature, the measurement temperature was adjusted to 25 ± 0.2°C using a thermostat jacket. The external diameter of the inner cylinder used for the rheometer was 25.0 mm, the internal diameter of the cup was 26.5 mm, and their gap was 1.5 mm. For measurement, the shear velocity was increased at a rate of 2.8 (1/s) per second until reaching 500 (1/s) in the inner cylinder, maintained at 500 (1/s) for 28 seconds, and was reduced at a rate of 2.8 (1/s) per second from 500 to 0 (1/s).

3. Results

The results of changes in the thixotropy of ERI containing 3% lithium magnesium sodium silicate (GE-100) are shown in Figure 1 and Table 1. In Figure 1, the dotted and solid lines indicate thixotropy before and that after

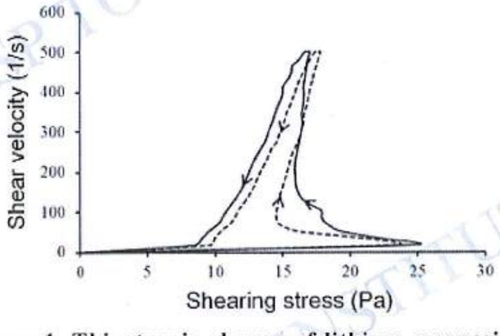

Figure 1. Thixotropic change of lithium magnesium sodium silicate gels prepared using electrolytic-reduction ion water (GE-100) sonicated by ultrasonication. Dotted line: before ultrasonication; solid line: after ultrasonication. Each linear arrow showed a direction of the hysteresis loop.

Table 1. Effect of ultrasonic treatment on hysteresis loop area of lithium magnesium sodium silicate gels prepared using GE-100

	Hysteresis loop area (Pa/s)	Area ratio (%)
GE-100 (before ultrasonication)	1,278 ± 33	100
GE-100 (after ultrasonication)	2,042 ± 67	160

GE-100: ERI containing 3% lithium magnesium sodium silicate. Mean ± SD, SD: standard deviation (n = 3).

ultrasonication, respectively. Shearing stress clearly increased after ultrasonication. In addition, as shown in Table 1, a comparison of thixotropy before and after ultrasonication showed a 60% increase in the hysteresis loop area rate after ultrasonication.

Subsequently, 0.1, 1, and 10% oil (jojoba oil, squalane, olive oil, or MCT) was added to GE-100, and the mixture was ultrasonicated. Changes in thixotropy are shown in Figure 2 and Table 2. In Figure 2, with an increase in the concentration of each type of oil, the shearing stress decreased. In Table 2 and Figure 3, the hysteresis loop area also decreased with an increase in the oil concentration. The rate (%) of the hysteresis loop area of GE-100 containing each type of oil to that of GE-100 alone (2,042 Pa/s) was the highest for MCT (143%) at a concentration of 0.1%, and the lowest also for MCT (58%) at a concentration of 10% (Figure 3). On the other hand, GE-100 containing olive oil showed high rates (134 and 103% at concentrations of 0.1 and 10 %, respectively).

Table 3 shows the zeta potential of oil droplets in each emulsion. GE-100 containing jojoba oil at concentrations of 0.1 and 1% showed low values (38.3 and –37.3 mV, respectively). However, the zeta potential did not markedly differ among the other types of emulsion (range: –23.4 - –26.8 mV).

The mean particle diameter of oil droplets in each emulsion is shown in Table 4. The mean particle diameter was small for olive oil (250-327 nm) and MCT (238-295 nm).

4. Discussion

Smectites basically have a 3-layer structure (tetrahedral layer-octahedral layer-tetrahedral layer) consisting of

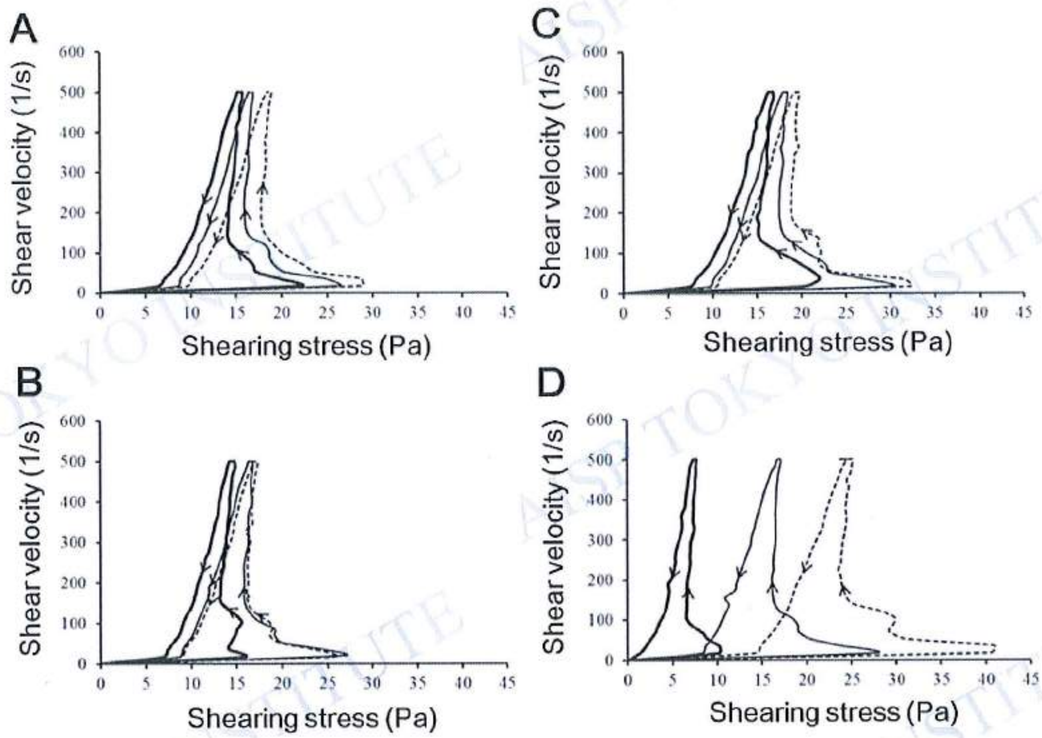

Figure 2. Thixotropic changes of different gels containing various oils. Dotted line: GE-100 + 0.1% oil; thin solid line: GE-100 + 1% oil; thick solid line: GE-100 + 10% oil. **(A)**: jojoba oil, **(B)**: squalane, **(C)**: olive oil, **(D)**: MCT. Each linear arrow showed a direction of the hysteresis loop.

Table 2. Thixotropic values of emulsions containing various oils

	Hysteresis loop area (Pa/s)		
GE-100 + Oil (%)	0.1%	1%	10%
GE-100 only	–	–	2,042 ± 67 (100)
GE-100 + jojoba oil	2,419 ± 138 (118)	2,219 ± 152 (109)	1,842 ± 62 (90)
GE-100 + squalane	2,039 ± 142 (100)	2,178 ± 129 (107)	1,485 ± 170 (73)
GE-100 + olive oil	2,741 ± 319 (134)	2,496 ± 64 (122)	2,101 ± 257 (103)
GE-100 + MCT	2,916 ± 377 (143)	2,301 ± 76 (113)	1,184 ± 124 (58)

( ): area rate (%); mean ± SD, SD: standard deviation ($n = 3$).

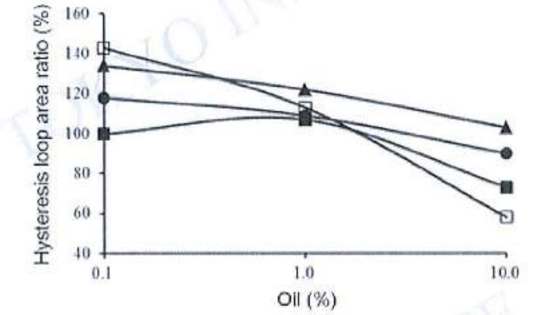

Figure 3. The relationship between the content rate (%) of various oils and hysteresis loop area. ●: GE-100 + jojoba oil, ■: GE-100 + squalane, ▲: GE-100 + olive oil, □: GE-100 + MCT.

Table 3. Zeta potential of oil droplets in various emulsions

GE-100 + Oil (%)	Zeta potential of oil droplets (mV)		
	0.1%	1%	10%
GE-100 + jojoba oil	-38.3	-37.3	-22.3
GE-100 + squalane	-26.9	-31.0	-26.4
GE-100 + olive oil	-26.1	-26.5	-25.2
GE-100 + MCT	-23.4	-30.5	-26.8

Table 4. Mean diameter of oil droplets in various emulsions

GE-100 + Oil (%)	Mean diameter of oil droplets (nm)		
	0.1%	1%	10%
GE-100 + jojoba oil	363 ± 329	573 ± 278	452 ± 244
GE-100 + squalane	355 ± 610	376 ± 832	471 ± 401
GE-100 + olive oil	250 ± 204	271 ± 267	327 ± 475
GE-100 + MCT	238 ± 182	266 ± 179	295 ± 299

Mean ± SD, SD: standard deviation (n = 220).

an octahedral sheet (composed of a magnesium atom coordinated by 6 oxygen atoms) sandwiched between 2 regular tetrahedral layers (composed of a silicate atom surrounded by 4 vertex oxygen atoms) (*1*). In lithium magnesium sodium silicate, due to the isomorphous substitution of some silicate and magnesium ions by lithium ions in the smectite structure, its surfaces are negatively charged, resulting in the formation of card-house structures. These card-house structures produce viscosity. The dispersion forms a gel with progression of card-house structures but forms a sol after shear force application, showing thixotropy. Lithium magnesium sodium silicate is widely used as a rheology modifier and texture enhancer, and particularly as a cosmetic material because it markedly increases viscosity and is highly thixotropic, well spread over the skin, and non-greasy (*13*). In this study, various types of oil were added to this GE-100, and the physiochemical characteristics of the emulsions were evaluated.

To evaluate the characteristics of GE-100 first, rheology measurement was performed before and after ultrasonication. As can be seen from Figure 1, thixotropy increased after ultrasonication. This may have been because honeycomb structures of lithium magnesium sodium silicate were more finely dispersed, resulting in denser binding.

Subsequently, various types of oil were added to GE-100 at 3 concentrations (0.1, 1, and 10%), and thixotropy was evaluated. With an increase in the concentration of each type of oil, the hysteresis loop concentration decreased (Figure 2). This was considered to be due to inhibition of the formation of card-house structures of lithium magnesium sodium silicate with an increase in the percentage of oil.

In addition, thixotropy was compared among GE-100 emulsions containing various types of oil at a concentration of 0.1 or 1% in terms of the rate (%) of the hysteresis loop area of GE-100 containing each type of oil expressed as a percentage of that of GE-100 alone (2,042 ± 67 Pa/s) (Table 2). As a result, at a low oil concentration, the hysteresis loop area rate was more than 100%, showing an increase in thixotropy. An increase in thixotropy indicates high viscosity in the static state and low viscosity after shear force application. When an emulsion is topically applied to the skin, oil added to GE-100 may allow maintenance of a highly viscous state, providing moisturizing effects, and also improve the viscosity and malleability. However, the hysteresis loop area rate was less than 100% in GE-100 containing each type of oil at a concentration of 10%. This suggested that the formation of card-house structures of lithium magnesium sodium silicate is prevented by oil with an increase in the oil concentration in GE-100. The hysteresis loop area rate was the lowest for MCT (58%). This may have been because MCT is medium chain fatty acid triglycerides of caprylic acid (8-carbon straight chain fatty acid), and its viscosity is lower than that of the other long chain fatty acids. At an oil concentration of 10%, the hysteresis loop area rate of 10% olive oil was high (103%) compared with the other types of oil. This may have been because olive oil is a long chain fatty acid mainly consisting of oleic acid (monounsaturated 18-carbon fatty acid), and, compared with MCT, the high viscosity of this oil itself affects thixotropy. At 20 °C, the dynamic viscosity of olive oil is about 85 mPa·s, on the other hand, that of MCT is about 23 mPa·s (*16*).

Comparison of the zeta potential showed low values in samples of GE-100 containing 0.1 or 1% jojoba oil (Table 3). Based on the Derjaguin, Landau, Verwey, Overbeek theory (DLVO theory) (*17,18*), these results suggest that the emulsion containing jojoba oil at a low concentration is more stable than the other emulsions.

The mean diameter of oil droplets was small in olive oil and MCT. According to the Stokes equation [I], the smaller the particle diameter, the lower the particle rise velocity. Therefore, emulsions of olive oil and MCT with a small particle diameter may be more stable.

$$v = \frac{d^2|\rho_0 - \rho|g}{18\eta} \qquad \cdots[\mathrm{I}]$$

(v: particle fall or rise velocity, d: particle diameter in the dispersed phase, ρ and ρ_0: densities of the dispersed phase and dispersion medium, respectively, g: acceleration of gravity, η: viscosity of the dispersion medium).

Based on these results concerning thixotropy and the particle diameter, when oil at a low concentration (0.1%) is added, MCT emulsions may be excellent in terms of texture and stability, and, when oil at a low (0.1%)-high (10%) concentration is added, olive oil emulsions may be excellent regarding texture and stability (Tables 2 and 4).

Concerning the reasons for the addition of oil to GE-100, when emulsions are applied to the skin, the moisturizing effects of oil can be expected (*19*). In addition, fat-soluble drugs can be added to the oil layer and used as bases for drugs for external use. In particular, as a general treatment method for atopic dermatitis, potent steroids are initially used and changed to weak ones with the alleviation of symptoms (*20*). However, as emulsifiers, synthetic surfactants such as sorbitan sesquioleate and glyceryl monostearate that markedly damage sensitive skin tissue are used. In addition, since drugs and cosmetics contain antiseptics such as paraoxybenzoic acid, which can cause allergic contact dermatitis and contact urticaria (*7*), there is a concern about the influences of their long-term use on the skin (*21*).

GE-100 used in this study is ERI containing lithium magnesium sodium silicate that is frequently used in cosmetics and improves the texture for topical application to the skin. To also add the moisturizing effects to this GE-100, oil was added, and emulsions were prepared. Various types of oil evaluated in this study are used in drugs, cosmetics, and foods. Emulsions obtained by adding each oil can prevent the influences of long-term use on the skin because of the absence of surfactants as well as the absence of the necessity of adding antiseptics due to the bactericidal effects of ERI (S-100) as the main solvent of GE-100 (*4*) or adding antioxidative agents such as dibutylhydroxytoluene, tocopherol, or ascorbic acid due to the reduction effects of ERI itself (*3*). Oil-in-GE-100 emulsions are expected to be new bases for external drugs.

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