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Stabilization of L-ascorbic acid in cosmetic emulsions

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ABSTRACT

The prevention of the oxidation of L-ascorbic acid in cosmetic emulsions was investigated. First, its stability was tested to determine the optimum ratio, and the effects of changes in the pH, color, and concentration of L-ascorbic acid in the emulsions were investigated. The kinetics of L-ascorbic acid in emulsions were studied through HPLC. The inclusion of glycerine in the dispersion was more effective in maintaining the initial L-ascorbic acid content than the inclusion of propylene glycol, butylene glycol or DI water. A zero-order reaction model best fitted the butylene glycol-in-oil emulsion, whereas a first-order model best fitted the water-in-oil emulsion.
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Introduction

Ascorbic acid is an enantiomer whose optical properties are classified as the L and D forms [1]. L-ascorbic acid (LAA), also called vitamin C, is a useful material in the human body [2]. The application of LAA to human skin provides many properties that improve the characteristics of the skin including whitening, wrinkle improvement and antioxidation. LAA can suppress the production of melanin, which makes skin darker, by aiding the reduction of melanin in the melanocytes; this is called the whitening effect [3,4]. In addition, LAA improves wrinkles by acting as a collagen synthesis coenzyme in the dermis [5]. Furthermore, LAA can prevent UV-induced damage to the DNA and proteins. Instead of reacting with DNA or proteins, the hydroxyl radicals derived from the reactive oxygen species that are generated by UV light react with LAA: this is called the antioxidant effect [6–8]. The efficacy of LAA is related to its oxidation. LAA is a type of reductone structure, as shown Fig. 1. Its oxidation occurs by first ionizing both hydroxyl groups at the second and third carbons of an enediol group and subsequently producing dehydroascorbic acid by the loss of 2 protons and 2 electrons [9–11].

Although LAA has many advantages, it is not generated in the human body. Hence, it must be acquired from an outside source via the skin or via oral administration: these sources include cosmetics, food, medicine and medical supplies [6]. In addition, LAA can easily be oxidized by external factors such as moisture, light, heat and metal ions. The oxidized form of LAA, dehydroascorbic acid, has no antioxidant effect because it cannot make ascorbate ions in the neutral pH of the human body [12].

Various studies of cosmetics, food, medical and medical supplies have attempted to prevent the oxidation of LAA by external factors [13–20]. The study of LAA derivatives is an especially active field. Percutaneous absorption of one LAA derivative, ascorbyl palmitate ascorbyl-2-glucoside, is less than that of ascorbic acid [15]. Additionally, magnesium-ascorbyl phosphate has a smaller antioxidant effect than LAA [16,17]. Therefore, the ability to stabilize LAA in an emulsion is critical for its effective delivery into the human body.

Two approaches have been generally applied to cosmetic materials. First, the structures of the materials can be changed to improve the effects and overcome drawbacks such as limitations in the skin permeation and solubility. Second, procedures to stabilize the effective materials in various emulsions have been developed. These two approaches are both important. However, the latter approach is preferred with respect to the time and the cost of developing cosmetic products. This approach should therefore be studied more thoroughly to create cosmetics that contain effective components.

Emulsion formulations can be classified as simple emulsions and double emulsions [21]. Simple emulsions are divided into the water-in-oil (W/O) and oil-in-water (O/W) types, which are characterized by a dispersed phase and a continuous phase. In contrast, double emulsions include the water-in-oil-in-water

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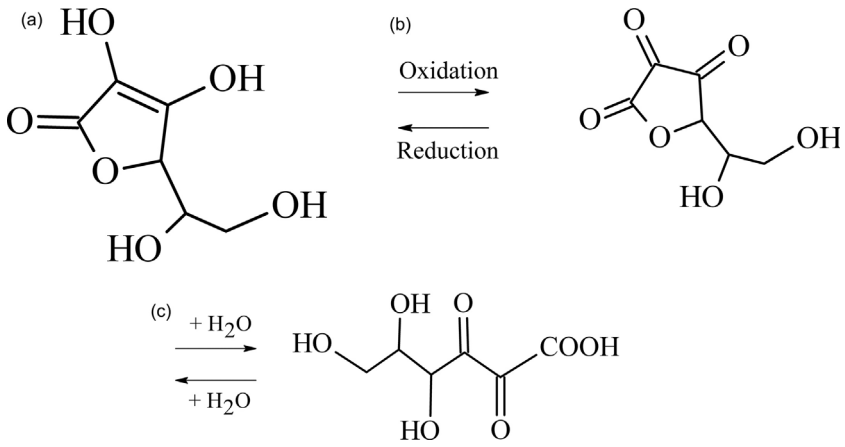

Fig. 1. Oxidation of LAA in aqueous solution: (a) LAA, (b) dehydro-LAA, and (c) 2,3-diketo-L-gulonic acid.

(W/O/W) or oil-in-water-in-oil (O/W/O) types. The type of emulsion used should be compatible with the target materials.

The present study used a simple emulsion process that involved monodisperse emulsion droplets rather than a double emulsion [22,23]. The process to formulate a simple emulsion is shorter than that required for a double emulsion, which minimizes the LAA oxidation during the emulsion formulation process. Additionally, this study was designed to assess the ideal raw materials to prevent the oxidation of LAA in the emulsions due to moisture. Four types of emulsions were used in this study: W/O, propylene glycol-in-oil (PG/O), butylene glycol-in-oil (B/O), and glycerine-in-oil (G/O) emulsions.

Another research group used LAA synthesized with a functional group or additives to stabilize the LAA. The safety and skin permeability of these materials in cosmetic emulsions were not efficiently confirmed [11,24]. Unlike the above-mentioned research group, we used polyol, which has been used as a moisturizer in cosmetic emulsions for many years and is a stable material in cosmetic emulsions. Therefore, the best material to stabilize LAA in cosmetic emulsions can be directly used in real cosmetic emulsions. Additionally, the expiration date of cosmetics containing LAA will be extended without the addition of preservatives for stabilizing the LAA.

Materials and methods

Materials

LAA was purchased from DSM (Havelock Road, Singapore). Glycerine was obtained from IOI Oleochemicals (Penang, Malaysia). Propylene glycol was purchased from SKC (Ulsan, Korea). 1,3-Butylene glycol was purchased from Daicel Corporation (Tokyo, Japan). Cyclohexasiloxane (SF1258) was purchased from Momentive (Seoul, Korea). Octamethylcyclotetrasiloxane (EA3105) was purchased from Elementis Specialties (Shanghai, China). Lauryl PEG-9 polydimethyl siloxyethyl dimethicone (KF6038) was purchased from Shin-Etsu Chemical (Tokyo, Japan). Sorbitan isostearate (Span™ 120) was purchased from Croda Korea Chemical (Seongnam, Korea). Cetyl dimethicone copolyol (Abil EM 90) was purchased from Evonik (Ulsan, Korea). Potassium phosphate (KH_2PO_4, monobasic, 99.0%) and phosphoric acid (H_3PO_4, 85%) were purchased from Samchun Chemical (Pyeongtaek, Korea). Deionized (DI) water was used throughout the study. All of the chemicals were reagent grade and were used without any further purification.

Preparation for emulsion formulations and change of color

To investigate the emulsion ratios for which no phase separation occurred, polyol-in-oil (P/O) emulsions were produced. Three kinds of polyols were used as the dispersed phase: glycerine, butylene glycol, and propylene glycol. The control formulation, a W/O emulsion, was prepared at the same ratio as the P/O emulsion.

Fig. 2 shows the emulsion formulation process. In the first step, the polyol used as the dispersed phase was weighed. Subsequently, LAA was added and was fully mixed using an agitator at 300 rpm for 5 min. For the next step, the continuous phase was produced from the oil, surfactant, and rheological additive. These solutions were mixed together with an agitator at 300 rpm for 5 min. Finally, the emulsion was created by adding the dispersed phase slowly to the continuous phase and mixing uniformly with an agitator at 500 rpm for 10 min. Instead of the polyol, DI water was used to make the control formulation using the same process as the P/O emulsions. All emulsions were incubated at 25 °C or 45 °C [25,26]. The time-dependent color changes of the emulsions were evaluated using a modified organoleptic method [27]. All emulsions stored under different conditions were investigated visually in terms of color and phase separation.

Determination of stability from phase separation

To select the best ratio for an emulsion, the W/O and P/O emulsions were stored at 25 °C or 45 °C. The phase separation of all emulsions over a period of 30 days was assessed using centrifugation (VS-5000i, Vision, Daejeon, Korea). Two grams of the sample was placed in a centrifuge tube, and a stability test was performed using the VS-5000i at 3000 rpm for 30 min. The sample was observed with respect to phase separation by visual examination [25].

Measurement of LAA content

The emulsions were incubated under storage conditions at 25 °C or 45 °C. The LAA content of each emulsion was confirmed using an HPLC system (Agilent 1260 Infinity, Agilent Technologies, Waldbronn, Germany). A 0.15 g aliquot of each sample was weighed and diluted to a final volume of 50 mL with 80% isopropanol (IPA). The diluted sample was subjected to ultrasonication for 20 min to completely dissolve the sample. After the sample was filtered, it was injected into a 2mL vial to measure the LAA content using HPLC.

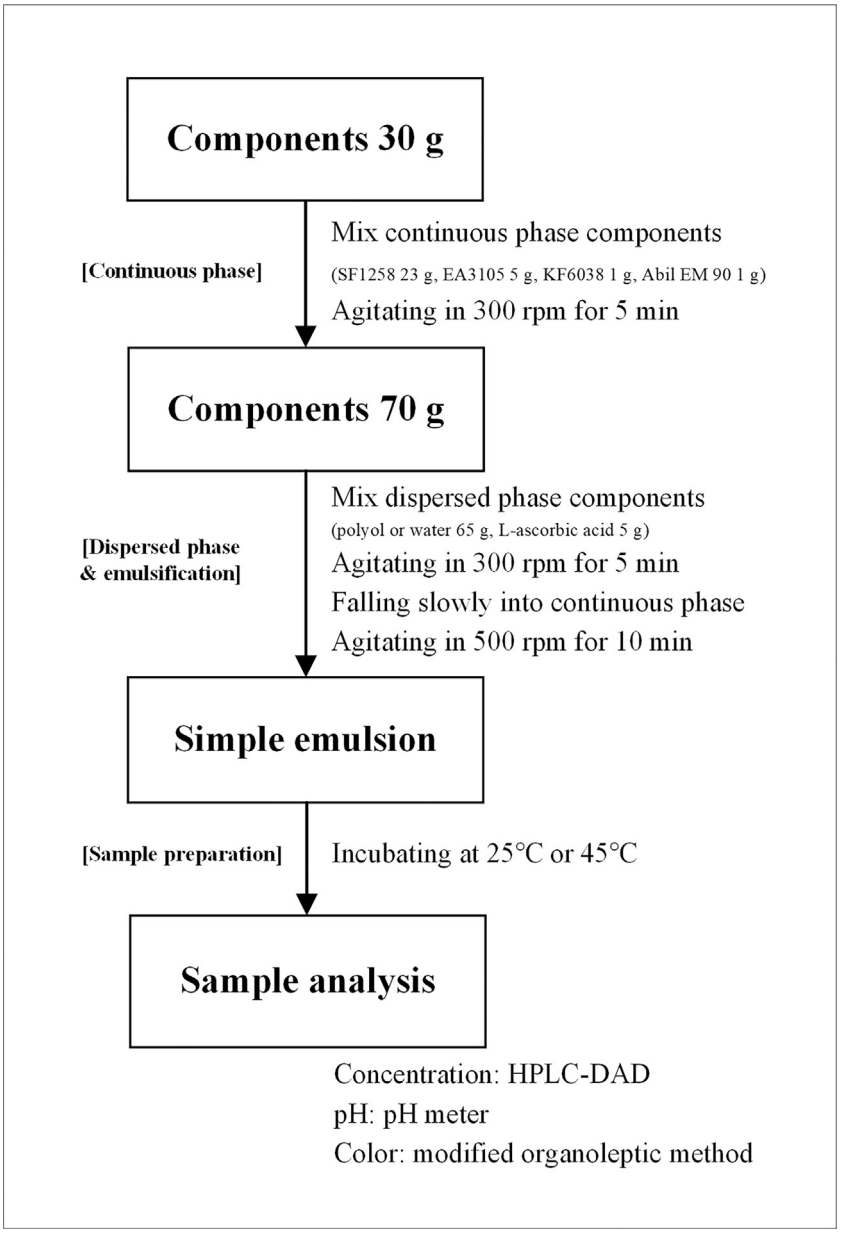

Fig. 2. Overview of the emulsion formulations.

The HPLC column used for the chromatographic separation was a reversed phase column (Zorbax Eclipse XDB-C18, 4.6 × 250 mm, 5 μm, Agilent Technologies, Santa Clara, CA, USA). The mobile phase was 0.2 M KH_2PO_4 with the pH adjusted to 2.4 with H_3PO_4. The flow rate was set to 0.5 mL/min using an isocratic pump. In addition, 0.5 μL was injected automatically by an autosampler [28,29]. The detector was a diode array detector (Agilent 1260 Infinity, Agilent Technologies, Waldbronn, Germany) set at 254 nm [28,30,31]. Under these conditions, LAA was detected at a retention time of 3.68 min. All experiments were repeated 3 times, and the mean values were calculated.

Kinetic study of the emulsions

The value r is the residual LAA in the emulsion. The ratio of measured LAA content (C_A) to initial LAA content (C_{A0}) was calculated using the following formula:

$$r = \frac{C_A}{C_{A0}} \times 100 \quad (1)$$

The general rate law was expressed by multiplying the concentration of reactant and the rate constant in the following formula [32]:

$$\frac{dC_t}{dt} = -k_c(C_t)^n \quad (2)$$

where t is the storage time, C_t is the LAA concentration at the measured time (t), and k_c is the rate constant, which depends on the experimentally determined order of the reaction (n).

The k_c can be predicted using the integrated rate law over time: zero-order, first-order, and second-order reactions. The following formulae are the integrated rate laws:

Table 1
Stability of polyol-in-oil (P/O) emulsions.

Components	Composition (wt %)	Composition (wt %)	Composition (wt %)	Composition (wt %)	Composition (wt %)	Composition (wt %)
Polyol[a]	65	65	65	65	65	65
L-ascorbic acid	5	5	5	5	5	5
SF1258	23	23	23	23	23	23
EA3105	5	5	5	5	5	5
KF6038	2	0	0	1	1	0
Abil EM 90	0	2	0	1	0	1
Span™ 120	0	0	2	0	1	1
Stability	MS	MS[d]	LS[c]	HS[b]	LS	LS

[a] Polyol = one of the three polyols, i.e., glycerin, butylene glycol, or propylene glycol, was used.
[b] HS = high stability.
[c] LS = low stability.
[d] MS = moderate stability.

$$\text{Zero-order: } C - C_0 = -kt \tag{3}$$

$$\text{First-order: } \ln C - \ln C_0 = -kt \tag{4}$$

$$\text{Second-order: } -\frac{1}{C} + \frac{1}{C_0} = -kt \tag{5}$$

The order of the degradation reaction can be predicted using a half-life time formula derived from the integrated rate law. The half-life time formulae are defined as follows:

$$\text{Half-life time of zero-order: } t_{1/2} = \frac{C_0}{2k} \tag{6}$$

$$\text{Half-life time of first-order: } t_{\frac{1}{2}} = \frac{ln2}{k} \tag{7}$$

$$\text{Half-life time of second-order: } t_{1/2} = \frac{1}{kC_0} \tag{8}$$

Determination of pH

The pH of the emulsions stored at 25 °C or 45 °C were measured using a pH meter (206-pH 2, Testo, Shenzhen, China). The pH of the emulsions kept at 25 °C was tested after 1, 10, 18, 25, 30, 40, 50, 60, and 70 days of storage, with the exception that the W/O emulsion, which was tested after 1, 10, 18, and 25 days of storage. The pH of the PG/O, B/O, and G/O emulsions maintained at 45 °C was checked after 1, 10, 18, 25, and 30 days of storage. The W/O emulsion was checked after 1, 5, 10, 15, and 21 days of storage. All experiments were repeated three times, and the mean values were calculated.

Results and discussion

Contents of the emulsion formulation

Table 1 shows for the outline of the experiment to identify a stable formulation that would not separate for at least 1 month. The ratio of the dispersed phase was determined experimentally to maximize the LAA content. This value accounted for 70% of the total amount. When the LAA content was over 7.14% of the dispersed phase, phase separation occurred. Therefore, the LAA content was fixed at 5% of the emulsion. The continuous phase contributed 30% of the whole emulsion.

In general, an emulsion can be prepared using only water, oil, and surfactant. However, the rheological additive EA3105 was necessary in the presence of LAA, which was likely because: (1) the dispersed phase was larger than the continuous phase and (2) a much lower surfactant ratio than the other existing emulsion formulation. EA3105 is made by dispersing hectorite in silicone. It improves the rheological properties of cosmetic emulsions through the phenomenon of bentonite swelling [33,34].

Three surfactants (KF6038, Span™ 120, and Abil EM 90) were used, and the amount of surfactant was constrained to 2%. One or two surfactants were used in the preparation experiments. The fractions of the surfactant in the dispersed phase and continuous phase can be predicted using the Bancroft rule [35], which determines whether a surfactant is soluble in the continuous phase. Although the dispersed phase made up 70% of the entire emulsion, the final continuous phase was oil because the surfactants were more soluble in oil. This result was consistent with the hydrophile-lipophile balance (HLB) value, which is particularly useful in an emulsion that contains a nonionic surfactant. Both Abil EM 90, which has an HLB value of 5, and KF6038, which has an HLB value of 3, were very soluble in oil. When these surfactants were added to the dispersed phase, the emulsion could not be created. Span™ 120 has an HLB value of 4.7. Although this value is similar to that of Abil EM 90, Span™ 120 contributed to phase separation of emulsion within 1 h when it was added either alone or in combination with another surfactant. Therefore, it was excluded from the final emulsion formulation.

To choose the optimum ratio for the final emulsion formulation, a stability test was performed using centrifugation. A mixture of surfactants did not lead to more separation than the use of a single surfactant. A physical mixture of Abil EM 90 and KF6038 was used: the ratio was 1:1. Table 2 describes the final composition of the emulsion formulations.

Time-dependent changes in the LAA content in the emulsions at 25 °C or 45 °C

The final emulsions were formulated as shown in Table 2 and were incubated at 25 °C or 45 °C. Fig. 3(a) shows the LAA contents of the W/O, PG/O, B/O, and G/O emulsions as functions of time. When the dispersed phase contained glycerine or propylene glycol, the LAA degradation was less than 40% for 100 days or more. These values were much lower than those observed when DI water or

Table 2
Final composition of the emulsions.

Components	Composition (wt%)
Polyol or water	65
L-ascorbic acid	5
SF1258	23
EA3105	5
KF6038	1
Abil EM 90	1

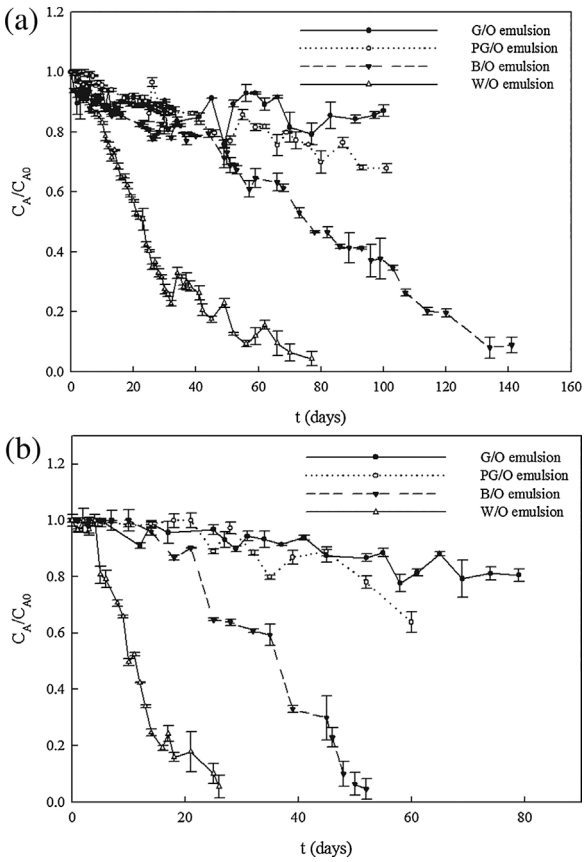

Fig. 3. The ratio of measured content of LAA (C_A) to initial content of LAA (C_{A0}) in emulsions (C_A/C_{A0}) vs. storage time (days) at: (a) 25 °C and (b) 45 °C.

butylene glycol was used as the dispersed phase. After 80 days, the LAA content decreased to less than 5% in the W/O emulsion. The LAA degradation was slower in the B/O emulsion than in the W/O emulsion. However, 65% of the LAA in B/O emulsion was oxidized after 100 days, and only 10% of the initial LAA remained after another 40 days.

Fig. 3(b) shows the LAA degradation in four different emulsions stored at 45 °C. The trends for the degradation were similar to those of the emulsions incubated at 25 °C. The LAA content in the W/O and B/O emulsions decreased more rapidly than that in the PG/O and G/O emulsions. The LAA content was less than 1% in both the W/O emulsion after 26 days and the B/O emulsion after 40 days. These results were likely due to the solubility of LAA in the various solvents with hydroxyl groups. The solubility of LAA increases with increasing numbers of hydroxyl groups in the solvent [36,37].

The color change of the W/O emulsion stored at 25 °C was remarkably fast, turning to pale yellow after 24 days. The colors of the PG/O, B/O, and G/O emulsions changed after 69, 66, and 90 days, respectively.

At 45 °C, the W/O, PG/O, B/O, and G/O emulsions changed color in that order. The W/O emulsion turned pale yellow after l day and became dark brown after 25 days. A yellow color appeared in the G/O emulsion after 17 days. Over the next 24 days, the G/O emulsion turned brown. The PG/O emulsion changed color after 14 days, whereas the color change of the B/O emulsion began at 18 days. After 18 days, the B/O emulsion changed color more quickly than the PG/O emulsion. Both emulsions turned dark brown after 30 days.

Table 3
Half-life and rate constants for L-ascorbic acid in water-in-oil (W/O) and butylene-in-oil (B/O) emulsion at 25 °C or 45 °C.

Emulsion type	T (°C)	Rate equation	R^2	k	$t_{1/2}$ (days)
W/O	25	$C - C_0 = -0.0719t$	0.87	0.072[a]	–
		$\ln(C/C_0) = -0.0394t$	0.96	0.040[b]	17.33
		$1/C_0 - 1/C = -0.0354t$	0.74	0.035[c]	–
	45	$C - C_0 = -0.2202t$	0.91	0.220[a]	–
		$\ln(C/C_0) = -0.1095t$	0.95	0.110[b]	6.30
		$1/C_0 - 1/C = -0.0894t$	0.70	0.089[c]	–
B/O	25	$C - C_0 = -0.0214t$	0.94	0.021[a]	118.50
		$\ln(C/C_0) = -0.0135t$	0.85	0.014[b]	–
		$1/C_0 - 1/C = -0.0049t$	0.73	0.005[c]	–
	45	$C - C_0 = -0.1003t$	0.95	0.100[a]	22.46
		$\ln(C/C_0) = -0.0503t$	0.77	0.050[b]	–
		$1/C_0 - 1/C = -0.0467t$	0.48	0.047[c]	–

[a] Unit = mmol L^{-1} day^{-1}.
[b] Unit = day^{-1}.
[c] Unit = $mmol^{-1}$ L day^{-1}.

Kinetic studies

Table 3 shows the results of the graphical analysis of regression functions created by fitting the integrated rate laws to the data for the W/O and B/O emulsions stored at 25 °C or 45 °C. The correlation coefficients (R^2) were compared to evaluate the reaction order.

The best fits for the experimental data for the W/O emulsion at 25 °C or 45 °C were observed using the equation for first-order kinetics, for which the R^2 values were 0.96 and 0.95, respectively. For the B/O emulsion, the experimental data were well-fit with zero-order kinetics. The R^2 values were 0.94 at 25 °C and 0.95 at 45 °C.

The half-life times for the W/O and B/O emulsions were investigated. The half-life times for the emulsions incubated at 25 °C were 17.33 days for the W/O emulsion and 118.5 days for the

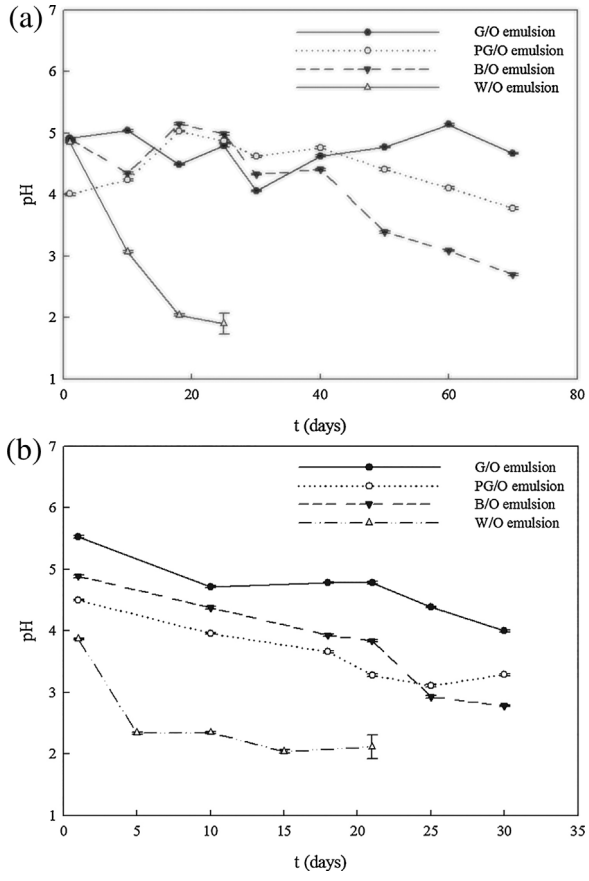

Fig. 4. pH in the emulsions vs. storage time (days) at: (a) 25 °C and (b) 45 °C.

B/O emulsion. These results indicate that butylene glycol slowed the LAA oxidization approximately 60-fold compared to the rate in DI water. When the emulsions were stored at 45 °C, the half-life times were 6.3 days for the W/O emulsion and 22.46 days for the B/O emulsion. The LAA in the B/O emulsion oxidized approximately 3 times more slowly than in the W/O emulsion. The kinetic constants increased for lower-order kinetics for all of the emulsions.

pH changes

As shown in Fig. 4(a), the pH values decreased with time at 25 °C. This trend was in close agreement with the degradation of the LAA content observed in Fig. 3(a). As expected, these results were caused by the oxidation of the LAA in the emulsions. The pH values declined with an increase in hydrogen ions. The hydrogen ions were released from the enediol group of LAA as a result of the oxidation process.

Fig. 4(b) shows the pH values of the emulsions stored at 45 °C, which decreased with time. As shown in Fig. 3, the LAA degradation was faster in the emulsions stored at 45 °C than in those stored at 25 °C. Similarly, the pH values gradually decreased over time.

The LAA content of the B/O emulsion decreased more quickly than that of the PG/O emulsion at 45 °C, as shown in Fig. 3(b). However, Fig. 4(b) shows that the B/O emulsion had a higher pH value than the PG/O emulsion.

Conclusions

This study was designed to identify materials that would contribute to LAA stability over time at 25 °C and 45 °C. The G/O emulsion that used glycerine as the dispersed phase retained the highest proportion of the initial LAA content over time, followed by the PG/O, B/O, and W/O emulsions. The kinetic results of the W/O emulsion incubated at 25 °C and 45 °C were fit well by a first-order reaction. However, for the B/O emulsion, zero-order reactions provided the best fit. At 25 °C, the pH values and the LAA content of the dispersed phase of the emulsion containing DI water, the W/O emulsion, decreased quickly; the pH values also decreased for the emulsions containing butylene glycol, propylene glycol, and glycerine. However, the rates of the decreases in the pH obtained for the PG/O, B/O, and G/O emulsions were slow. This result was consistent with the LAA degradation. At 45 °C, the pH values for the W/O emulsion decreased more rapidly than those of the other emulsions, with the order PG/O, B/O and G/O. In particular, the PG/O emulsion and B/O emulsion had strongly different trends for the degradation of the LAA. In conclusion, glycerine and propylene glycol are useful for preserving LAA in cosmetic formulations.

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