Colloids and Surfaces B: Biointerfaces 154 (2017) 307–314

Contents lists available at ScienceDirect

Colloids and Surfaces B: Biointerfaces

journal homepage: www.elsevier.com/locate/colsurfb

Spreading properties of cosmetic emollients: Use of synthetic skin surface to elucidate structural effect

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ARTICLE INFO

Article history:
Received 20 November 2016
Received in revised form 17 February 2017
Accepted 13 March 2017
Available online 16 March 2017

Keywords:
Spreadability
Emollients
Esters
Contact angle
Viscosity
Surface tension

ABSTRACT

The study focuses on the impact of structural and physicochemical properties of emollients on their spreadability. Fifty-three emollients, among which esters, silicones, vegetable and mineral oils, have been characterized. Their viscosity, surface tension, density and spreadability have been measured. Vitro-skin®, an artificial skin substitute, was used as an artificial porous substrate to measure spreadability. Two different methods have been selected to characterize spreadability, namely contact angle and spreading value. Dynamic contact angle measurements showed that emollient spreadability is first governed by spontaneous spreading and that, in a second phase, absorption and migration into the porous substrate becomes the driver of the extension of the spreading area. Statistical analysis of physicochemical and spreading value data revealed that viscosity has a major impact on the spreading behavior of emollients whatever their chemical type. A special emphasis was placed on the ester family in which chemical diversity is very wide. The results highlighted a difference between "high viscosity esters" for which viscosity is the main factor impacting spreadability and "low viscosity esters" for which structural variations (mono/diester, saturated/unsaturated chain, linear/branched chain) have to be considered in addition to viscosity. Linear regressions were used to express spreading value as a function of viscosity for each of the four emollient families tested (esters, silicones, vegetable and mineral oils). These regressions allowed the development of reliable predictive models as a powerful tool for formulators to forecast spreadability of emollients.

1. Introduction

Emollients are one of the most important and broad classes of ingredients used in personal care formulations [1]. In addition to their moisturizing and protective effects [2–4], emollients are particularly used to adjust the consistency, spreading properties and skin feel of cosmetic formulas [5]. As they are often the largest non-water component of skin care emulsions [1,6], they have a major impact on the features and performance of the product [7–9].

The term "Emollient" refers to a great diversity of substances commonly classified according to their chemical structure: esters, silicones, vegetable oils, fatty alcohols, mineral oils, synthetic hydrocarbons... In each group a wide range of sensory, physicochemical and functional properties are available thanks to diverse structural variations. Depending on the emollient family, these structural variations may concern chain length, degree of polymerization, presence of branching or of cyclic structure, degree of unsaturation, presence or substitution of functional groups... [10,11,4]. To date, the influence of this great chemical and structural diversity on the spreading properties of emollients has not been reported.

Spreadability of a cosmetic emollient can be defined as its capability to cover an area of skin more or less quickly on the skin [12,13]. Several studies have attempted to characterize the spreading properties of cosmetic emollients, either pure [5,6,8,11–14] or in complex emulsions [7,13]. To achieve this goal, various methods have been used, especially: contact angle measurement [6,11,13–15], spreading value evaluation [2,6,12,13], texture analysis [13] and sensory analysis [5–8,13,17]. Some studies measured *in vivo* spreadability on human skin [12,13,16] while some others used artificial substrates like Poly(methyl methacrylate) (PMMA) [13] or silicone rubber [6,19] to carry out measurements. The present study compares two methods using Vitro-skin® [6,11,17] as model substrate and provides an efficient tool to evaluate the spon-

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http://dx.doi.org/10.1016/j.colsurfb.2017.03.028
0927-7765/

taneous spreading and adsorption of a wide range of emollients owing to their different physicochemical properties.

Several authors have attempted to correlate spreadability with the physicochemical properties [5,6,8,11–13] of liquids. Most studies established a clear anti-correlation between viscosity (or its logarithm) and spreadability [6,11–13]. It was also demonstrated that liquids with lower surface tension exhibit higher spreadability [12,18]. The impact of density has been less studied. However, to our knowledge only very few attempts have been made to compare and rank the impact of these three physicochemical properties.

In 1985, Zeidler [12] characterized 29 emollients (esters, vegetable oils, mineral oils, alcohols, hydrocarbons) and investigated the relationships between the spreading behavior and the physicochemical and chemical properties of emollients. Nevertheless, the author did not explore the impact of chemical structure variations for a given family. More recently, Hughes et al. [11] identified chemical structure/property relationships by comparing 20 emollients. However, the author based his observations on the analysis of only one pair of homologous molecules, which is probably not sufficient to draw reliable conclusions. Thus, the link between chemical and structural properties of emollients and their spreading behaviors still remains misunderstood.

The aims of this study were thus (a) to identify and rank the impact of the physicochemical properties of emollients on their spreading behavior and (b) to investigate the effect of chemical and structural variations on emollients' spreadability. For this purpose 53 emollients, either esters, silicones, mineral and vegetable oils, were selected among the most commonly used in the cosmetic field. The physicochemical properties of these ingredients, namely viscosity, surface tension and density, were measured. In addition, spreading ability was characterized using two different methods: sessile drop contact angle measurement on the one hand and spreading value evaluation on the other hand. Partial Least Square (PLS) was then used to evaluate the respective impact of viscosity, density and surface tension on spreadability. Finally, simple linear regressions were conducted to study and model the effects of both chemical and structural properties of emollients. The strength of the present work relies on a statistical and rigorous comparison of the properties of a large number of emollients.

2. Material

2.1. Materials: ingredients used

A total of 53 cosmetic emollients belonging to 4 different chemical families have been characterized: 37 esters, 5 silicones, 5 mineral oils and 6 vegetable oils (see Table 1).

All these cosmetic grade ingredients were kindly given by raw material suppliers: Stéarinerie Dubois (France), Croda (UK), Aiglon (France), Wacker (US), Bluestar silicone (France), Bertin (France), Olvea (France), Provital (Spain).

2.2. Characterization of spreading behavior

2.2.1. Selection and conditioning of an adequate substrate

Vitro-skin® (IMS, Milford, CT), an artificial skin substitute, was chosen for spreading property measurements.

Vitro-skin® needs to be hydrated prior to use. To obtain proper hydration, a standardized hydration protocol has been developed by IMS: Vitro-skin® pieces have to be placed during 16–24 h on the shelf of a standardized hydration chamber containing 350 g of a 14.85%w/w glycerin/water mixture at the bottom.

2.2.2. Evaluation of spreading value

Spreading value was defined as the surface area covered by 10 μL of emollient. The liquid was deposited in the center of a hydrated 65 × 65 mm piece of Vitro-skin® using a micropipette. The Vitro-skin® specimen was kept in the hydration chamber for 10 min, corresponding to the spreading phase. After 10 min, wheat flour was deposited on the substrate and the excess of non-adherent flour was removed thus revealing the outline of the spreading zone; the specimen was photographed, and the exact area of this spreading zone was determined by image analysis of each specimen using a computer program (Image J, Wayne Rasband, National Institutes of health, USA). Measurements were performed in duplicate, at room temperature. Spreading values were expressed in mm^2. The higher the spreading value, the better the emollient spreads.

2.2.3. Dynamic contact angle measurement

Spreading behavior of emollients was characterized using dynamic contact angle measurements (Digidrop GBX goniometer). A pendant drop of liquid was formed with a syringe until it was large enough to fall gently onto a 20 × 40 mm Vitro-skin® specimen fixed on a PTFE (Teflon®) horizontal basement. The distance between the needle of the syringe and the substrate was about 5 mm, to ensure that the drop momentum was negligible. Images of the spreading droplet were captured by a digital camera (25 images/sec), from the initial deposit to the maximum spreading corresponding to a constant contact angle. Contact angle, base area and droplet volume over time were monitored using the GBX software Windrop++. Measurements were done at room temperature. The reported values correspond to the mean of at least 3 repeatable measurements. The lower the contact angle, the better the emollient spreads.

2.3. Characterization of physicochemical properties

2.3.1. Density

Emollient density was measured in triplicate with a portable densimeter (Mettler Toledo, France). Prior to measurement, the ingredients were conditioned at 25 °C using a water-bath for at least one hour.

2.3.2. Viscosity measurement

Measurements were done using an AR2000 rheometer (TA Instruments, US) fitted with an acrylic cone-and-plate geometry (2°1′53″ cone angle, 60 mm diameter, 52 μm gap) and using a continuous flow procedure ranging from 0.1 to 100 s^{-1} (log mode) for 2 min. Viscosity value is the average of the values reported from the curve representing the viscosity as a function of shear rate.

Viscosimetric measurements were performed using an AMVn falling-ball viscometer (Anton Paar, Austria) when emollient viscosity was lower than 25 mPa s. Measurements were made with a steel ball of 1.5 mm diameter and a glass capillary of 1.6 mm diameter with rolling angle of 45°.

All measurements were done at 25 °C, in duplicate.

2.3.3. Surface tension measurement

Surface tension was measured at room temperature using a K11MK4 tensiometer (Krüss, Germany) equipped with the standard Du Noüy ring accessory (wire diameter:0.370 mm; ring diameter:19.09 mm). Reported surface tension corresponds to the average value of five measurements.

2.4. Data analysis

Statistical analyses and mathematical modellings were performed using XLSTAT® software (2012.1.01 version, Addinsoft, Paris, France).