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International Journal of Pharmaceutics 256 (2003) 75–84

international journal of pharmaceutics

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Study of the structure of coherent emulsions

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Received 30 July 2002; received in revised form 13 December 2002; accepted 23 December 2002

Abstract

The object of the study was to analyse relationship between the rheological properties, thermogravimetric behaviour, physical stability, and the wetting contact angle of the lipophilic and aqueous phase of 300 creams of different compositions with a high water content (60–80%, w/w). The starting point was Junginger's theory: water is found in the cream structure in energetic (interlamellar) and steric forms (bulk water). Based on our investigations, an exponential function was found to exist between the contact angle of wetting and the slope of the TG-curves, between the contact angle of wetting and the viscosity of the creams, and between the contact angle of wetting and the evaporation rate of water. A linear relationship was found between the contact angle of wetting and the quantity of water separable by centrifugation.

Keywords: Cream structure; Contact angle; Rheology; Thermal analysis; Evaporation of water

1. Introduction

Coherent emulsions are of three different types: (i) creams (washable and unwashable ointments with water content); (ii) gel emulsions; and (iii) microemulsion gels. Their typical property is that they have a yield value and a thixotropic rheological character. When deformed with slight shear stress, they exhibit a viscoelastic character. The present study is focusing on coherent-structured gels with a high water content belonging to the first group.

These systems represent the most important vehicles in dermatological and cosmetic preparations, so quite understandably they have been in the foreground of pharmaceutical technological research for a long time. The scientific study of the cream structure was started in the 1950s, with the examination of the so-called "invisible" structure that is the rheological character (Münzel and Ammann, 1955a,b, 1956).

The research of creams can be divided into three steps, which cannot be separated in time and overlap each other. The first step is constituted by the use of rheological methods. In addition to the exact description of the rheological character, the role of surfactants in the formation of a coherent structure (Elworthy and Florence, 1967; Talman et al., 1968; Talman and Rowan, 1970), the role of the emulsified water in the structure (Richter and Kadner, 1969) and the effect of the increasing water quantity on the rheological properties (Erős and Ugri-Hunyadvári, 1977; Erős et al., 1980; Kedvessy et al., 1982; Erős and Kedvessy, 1984; Taleb and Erős, 1996) were elucidated with rotational and oscillatory viscosimetric examinations. The second step was the introduction of optical and electronoptical methods (Gstirner et al., 1969; Barry, 1971; Müller-Goymann and Führer, 1987; Müller-Goymann, 1984, 1987), the use of X-ray diffraction (Führer et al., 1978; Junginger et al., 1979) and the application of thermal analysis. With the help

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doi:10.1016/S0378-5173(03)00064-4

of thermal analysis it was clarified that water is fixed in the structure basically as (i) interlamellarly bound water, and (ii) bulk water (Junginger, 1984a,b). The third step of research was constituted by the development of structural theories. In the first scientific theory, the coherent structure of creams was explained by the formation of complex-emulsifier pairs (Münzel and Berneis, 1969). According to Barry's theory, the structure of systems consisting of surfactant, long carbon-chain alcohol and water is a solidified liquid crystalline structure (Barry, 1971). The lamellar theory about the microstructure of creams was set up by summarizing the results of X-ray diffraction, microscopic, electron microscopic, thermoanalytic, differential scanning calorimetric, and rheological studies. According to this, amphiphilic components (surfactants, long carbon-chain fatty alcohols) have a lamellar structure. Water representing the external phase of creams, therefore, can be found between the bilayer, bound in the gel phase or exists as bulk water (Junginger, 1984a,b; Eccleston, 1986).

Significant attention is being focused on the structural examination of creams today, too. Noteworthy and important results have been achieved with the simultaneous application of rheology and thermogravimetry (Peramal et al., 1997), rheological methods make it possible to select the optimum surfactant combinations (Korhonen et al., 2000, 2001), and in structure research a new perspective is represented by neural network modeling (Gašperlin et al., 1998). Drug release is another important field of research (Laugel et al., 1998; Erős et al., 2000; Clément et al., 2000).

In addition to the above overview, important research made by several other authors could be mentioned. However, only results serving as the direct experimental preliminaries to our research were included.

In spite of the great number of research results, the formulation of creams, the selection of major components of structure formation and the determination of the surfactant concentration are still performed experimentally.

The following aims were set in our experiments:

(i) A simple and rapid method was searched for the measurement and for the numerical description of the major components of structure formation. In our previous studies wetting between the hydrophilic and lipophilic phases of creams was found to be the most important factor of structure formation (Mednyánszky, 1984). For this reason the contact angle, which gives the quantitative description of wetting between the lipophilic and hydrophilic phase, was studied thoroughly in appropriate model experiments.

(ii) Detailed studies were performed to find out how the contact angle of the wetting of the two phases with opposite polarity influences the binding of the water phase in the gel structure. The evaporation rate of the water phase was studied using differential thermoanalysis and a relationship was searched between the wetting contact angle and the bond energy of water.

(iii) The relationship between the rheological properties (parameters describing the "invisible" structure of coherent systems) and wetting was studied.

(iv) The relationship between individual components of stability (e.g. evaporation of the aqueous phase, temperature dependence of the viscosity of creams, quantity of water separated by centrifugation) was studied in detail.

2. Experimental

2.1. Materials

The lipophilic phase of the creams consisted of white petrolatum (Vaselinum album Ph. Hg. VII.) and cetyl-stearyl-alcohol (Alcoholum cetylstearylicum, (Ph. Hg. VII., Eu. Pharm. 4)). Distilled water and 1% hydroxy-ethyl-cellulose (hydroxyaethylcellulosum, Ph. Hg. VII.) solution served as the aqueous phase. The following emulsifiers were used: Tween 20, 40, 60, 80 (Uniqema); Tagat S, S2, O, O2, L, L2, TO, R40, Emulgator BTO (Goldschmidt AG, Germany); Cremophor, A6, S9, Rh40, RH60, (BASF, Germany); Eucarol AGE/EC, AGE/ET, AGE/SS (Lamberti SpA, Italy). The concentration of the emulsifiers was 3, 5, and 10% (w/w) (Table 1).

2.2. Methods

Quantitative description of wetting: a uniform film of the lipophilic phase was formed on a glass plate.

Table 1
Composition of studied creams

Components	Series 1					Series 2					Series 3				
Amount in % (w/w)															
Cetyl-stearyl-alcohol	10	10	10	10	10	5	5	5	5	5	5	5	5	5	5
White petrolatum	27	22	17	12	7	30	25	20	15	10	25	20	15	10	5
Surfactant	3	3	3	3	3	5	5	5	5	5	10	10	10	10	10
Distilled water[a]	60	65	70	75	80	60	65	70	75	80	60	65	70	75	80

[a] Containing 0.1% methy-*para*-hydroxi-benzoate.

Emulsifier-containing water was dropped onto the lipophilic phase from a microburette and the arising contact angle was determined using Lerk's method and apparatus (Lerk et al., 1976). The Weber–Wolfram equation was used to calculate the contact angle (Wolfram, 1971).

The rheological examinations were performed using Rheometer MC1 (Paar Physica) apparatus and Rheostress 1 apparatus (Haake KG). The complete yield and viscosity curves were drawn and the yield values as well as the initial and equilibrium viscosity were determined.

Thermoanalysis was carried out with the MOM apparatus (MOM Derivatograph C). The TG-, DTG- and DTA-curves were drawn. The energy of the water binding was described with the slope of the TG-curves.

The stability of the systems was analyzed on the basis of the evaporation of the aqueous phase and centrifugation experiments data. Evaporation was examined gravimetrically in a desiccator of a constant moisture content. Centrifugation experiments were performed with a Janetzki K-23 apparatus at 5000 rpm for 30 min. The physical stability of creams was described with the separation of the aqueous and oil phases and with the volume of the separated water. The order of the performed examinations is given in Fig. 1.

The following relationships were studied:

- contact angle of wetting versus structural viscosity;
- contact angle of wetting versus the slope of the TG-curves (in the temperature range of 25–85 °C);

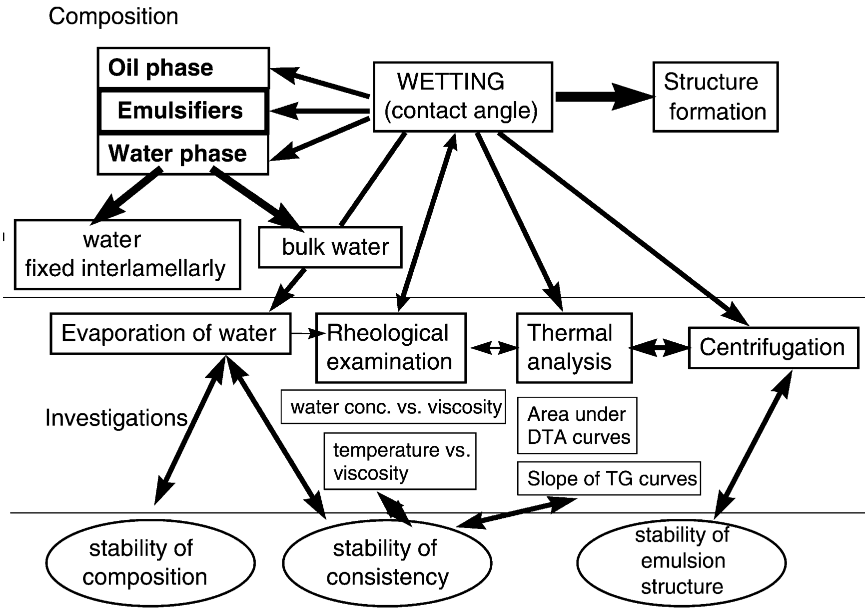

Fig. 1. Order of experiments. Elements and sections of investigations.

- contact angle of wetting versus the slope of viscosity–water concentration functions;
- contact angle of wetting versus the evaporation rate of the aqueous phase;
- contact angle of wetting versus the thermostability of viscosity;
- contact angle of wetting versus water separated by centrifugation (physical stability).

3. Results and discussion

3.1. Structure formation and rheological studies

Based on their rheological character, the studied creams (300 creams of different compositions) were viscoelastic and thixotropic systems with a yield value (in the shear rate range of 0.1–500 l/s). The thixotropic character is illustrated in Fig. 2. The flowcurves of 5% (w/w) Eucarol and 60–80% (w/w) water-containing creams are shown in Fig. 2.

The viscosity of the creams is a numerical characteristic of forces acting in the coherent structure: the greater the forces in the coherent lipophilic phase, the greater the viscosity of the cream. Viscosity was found to show a characteristic increase with the increase of the contact angle (Fig. 3).

This increase can be described with an exponential function:

$$\eta = \eta_0 \exp(a\Theta) \qquad (1)$$

where η, the initial viscosity of gels (mPa s); η_0, viscosity pertaining to 0 wetting; Θ, contact angle of wetting (°).

This phenomenon can be explained with the frame elements hydration. More hydrated gel frame (increasing amount of water bound in the lamellar space) results in lower wetting contact angle and creams with softer consistency characterized by lower structural viscosity. The background of poor wetting is that less water is fixed interlamellarly and the ratio of bulk water is higher, resulting in a higher viscosity.

A relationship was found not only between viscosity and wetting, but also between the constant of the viscosity function and water content and the wetting contact angle (Fig. 4).

According to our studies the viscosity of hydrophilic creams shows a characteristic decrease with the increasing water content. This decrease can be described

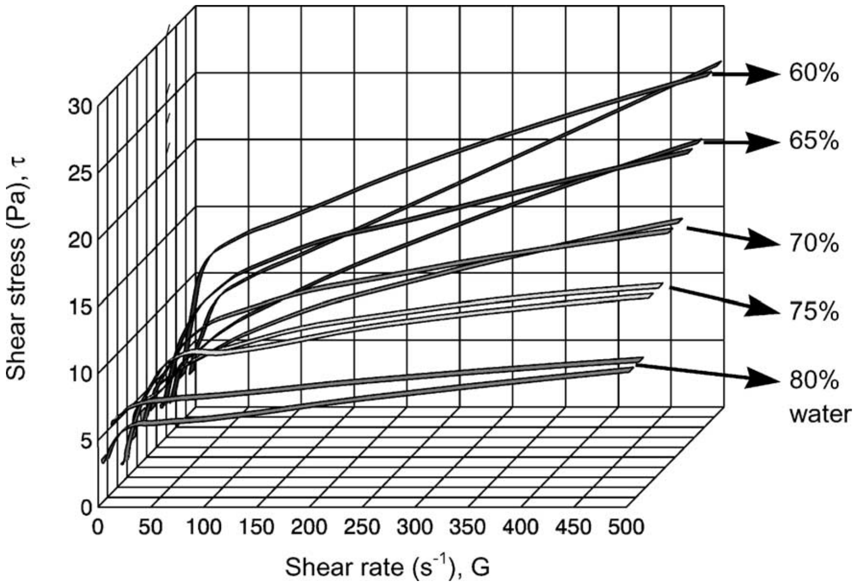

Fig. 2. Flow curves of creams containing different concentration of water. (Composition: Series 2, emulsifier: Eucarol AGE/SS in 5% (w/w), distilled water: 60–80% (w/w).)

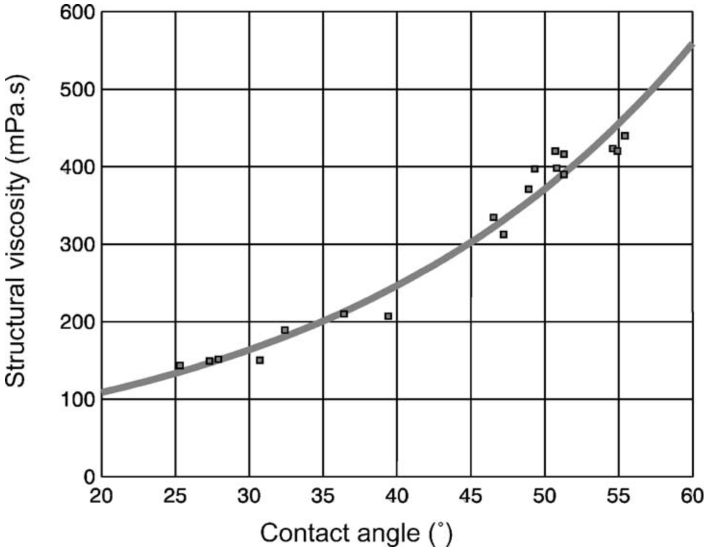

Fig. 3. The effect of wetting on the structural viscosity of creams. (Results of 18 compositions, concentration of emulsifiers: 5% (w/w), concentration of water: 70% (w/w).)

with an exponential function

$$\eta = \eta_0 \exp(-mc) \tag{2}$$

where η, the initial viscosity of creams; η_0, the viscosity of systems with 0 water concentration; c, the concentration of emulsified water (w/w%); m, constant.

The slope of the function (m) shows how water is bound in the gel structure. If a substantial quantity of water is in energetic binding (closed interlamellarly)

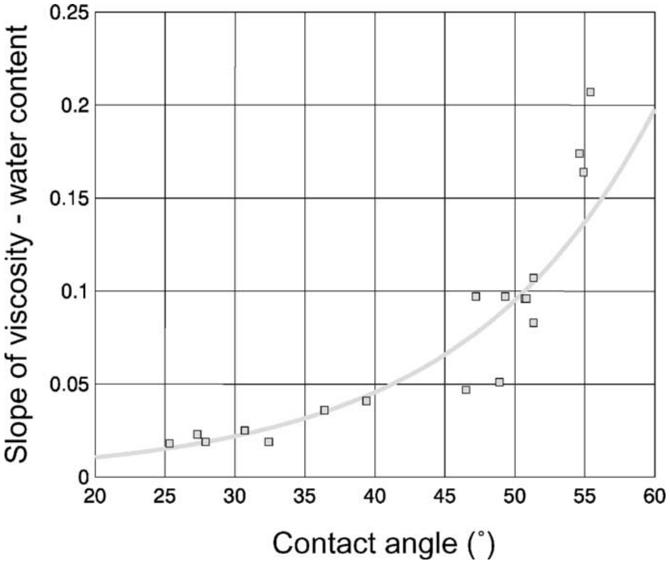

Fig. 4. The effect of wetting on the structure formation constant. Structure formation constant can be calculated from the relationship between structural viscosity–water concentration (Mednyánszky, 1984). The slope of this linearized exponential function can be considered as the structure formation constant. (Total 18 compositions, concentration of emulsifier: 5% (w/w), concentration of water: 60–80% (w/w).)

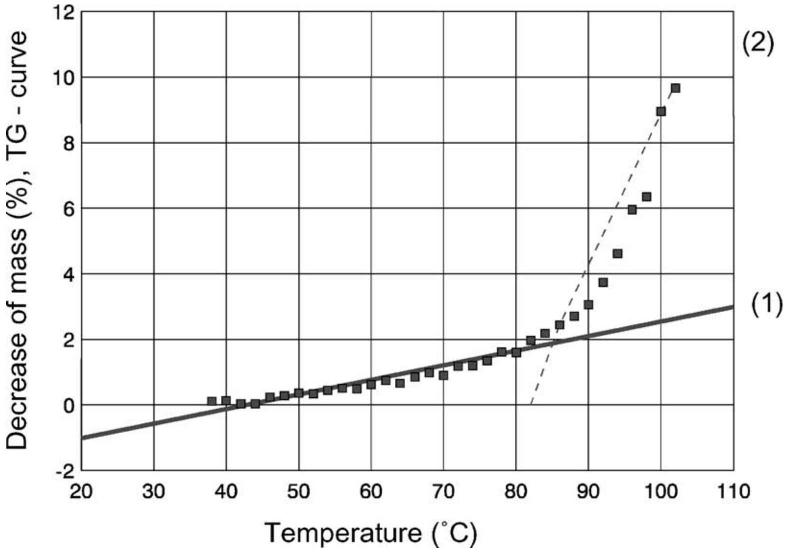

Fig. 5. TG-curve of cream containing 5% (w/w) Eucarol AGE/SS and 80% (w/w) water.

and only a smaller quantity is in mechanical binding (bulk water), the slope of the functions is a constant of a small numerical value.

In our studies an exponential relationship was also found between the constants of the water concentration–viscosity functions (m) and the contact angle:

$$m = m_0 \exp(b\Theta) \tag{3}$$

where m, the slope of the viscosity–water concentration functions (Eq. (2)); Θ, the contact angle of wetting; b, the constant of the function. Constant b expresses the extent of viscosity increase accompanying the increase of contact angle unit.

3.2. *Examination of the aqueous phase binding by thermoanalysis*

The most efficient method for the examination of the water phase binding is the thermogravimetric method (Junginger, 1984a,b). The TG-curve of differential thermoanalysis (Fig. 5) shows the mass change (probably the decrease of water content) with the temperature increase.

Our results show that the TG-curves consist of two sections with different slope. The first section has a lower slope, the second section a higher one and they can be described with the following functions:

$$\Delta m_1 = \Delta m_0 + a_1 T_{(20\text{–}85)} \tag{4}$$

$$\Delta m_2 = \Delta m_0 + a_2 T_{(85\text{–}100)} \tag{5}$$

where Δm, mass decrease; m_0, and a, constants; T, temperature.

A characteristic relationship was found between the slope of the first section (a_1) and the wetting contact angle: the poorer the wetting (the greater the contact angle), the greater the evaporation rate of water. Therefore, the quantity of the energetically (interlamellarly) bound water can be deduced from the extent of wetting. This function is also an exponential equation (Fig. 6):

$$a = a_0 \exp(c\Theta) \tag{6}$$

where a, the slope of the first section of the TG-curve; Θ, contact angle; a_0 and c, constants.

3.3. *Stability of creams and wetting*

Two factors were studied with respect to the stability of creams: (i) the evaporation of the water phase, and (ii) separation due to centrifugation.

During the evaporation studies the water content of creams was found to decrease according to a

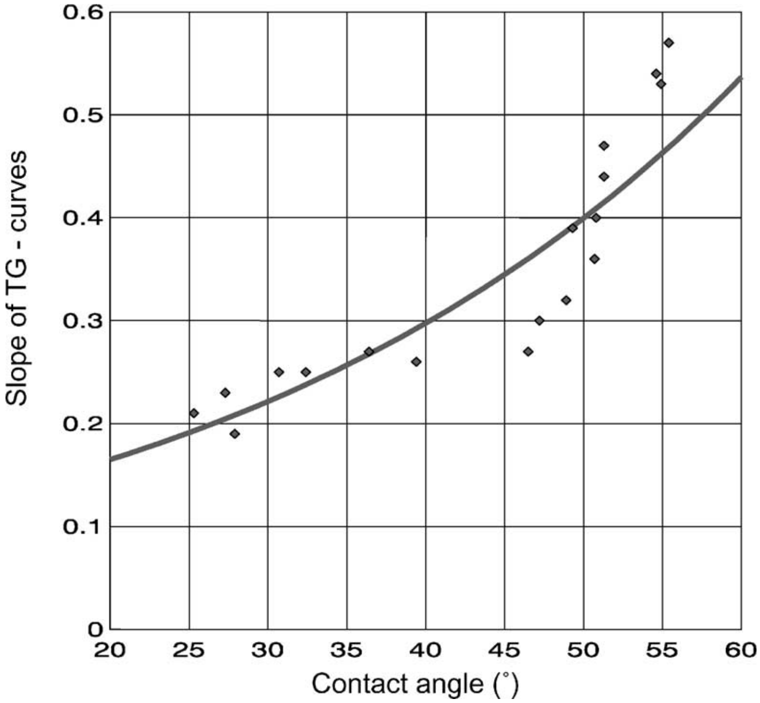

Fig. 6. The effect of wetting on the evaporation of water under heat. (The slope of first section of TG-curves, based on Eq. (4)). (Total 18 compositions, concentration of emulsifier: 5% (w/w), concentration of water: 70% (w/w).)

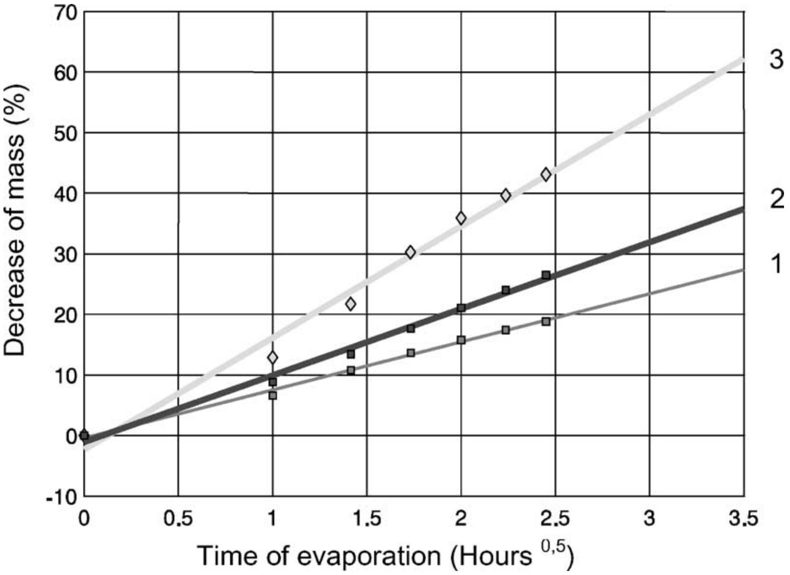

Fig. 7. Kinetics of water evaporation from creams containing different emulsifiers. (1) Eucarol AGE/ET, (2) Cremophor A6, (3) Tween 80.

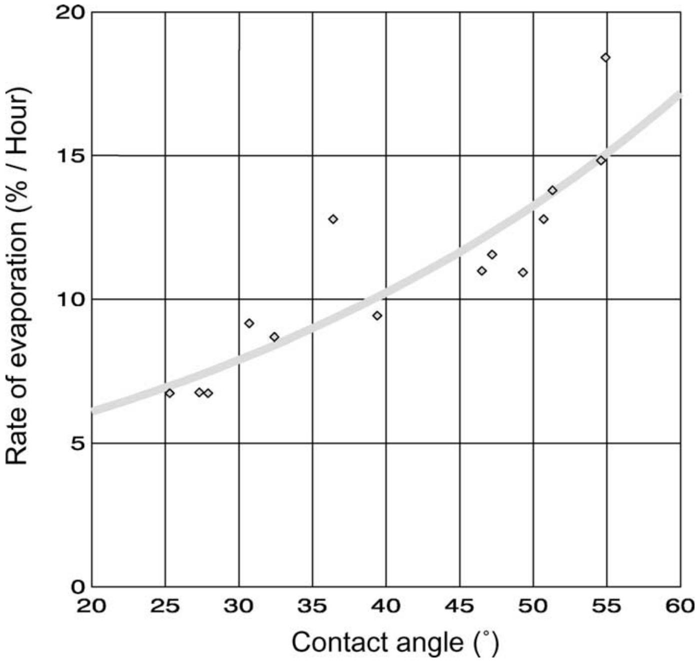

Fig. 8. The effect of wetting on water evaporation rate (calculation is based on Eq. (7), 14 composition, emulsifier: 5% (w/w) and 10% (w/w), concentration of water 70 and 80% (w/w)).

well-defined function (Fig. 7):

$$\Delta w = \Delta w_0 + d(t)^{0.5} \tag{7}$$

where Δw, mass decrease; t, examination time; w_0 and d, constants.

The evaporation of water is in correlation with wetting: the smaller the energy of water binding, the greater the extent of the water evaporation of the cream. This relationship can also be described with an exponential function (Fig. 8):

$$d = d_0 \exp(g\Theta) \tag{8}$$

where d, the evaporation rate of water (slope of Eq. (7)); d_0 and g, constants; Θ, the contact angle of wetting.

An exact description of physical stability is given by the amount of water separated by centrifugation. The quantity of the separated water–contact angle function is given in Fig. 9. A linear relationship was found between this element of physical stability and the contact angle:

$$S = S_0 + n\Theta \tag{9}$$

where S, the quantity of the separated water; Θ, the contact angle of wetting; S_0 and n, constants.

The correlation coefficients of the contact angle functions (Eqs. (1), (3), (6), (8) and (9)) are summarized in Table 2. These constants prove that wetting characterized by the contact angle is a decisive factor in the structure formation.

Table 2
Relationship between wetting of hydrophilic and lipophilic phases and properties of creams

Wetting	Properties of creams	Function	Correlation coefficient	Figure	Equation
Contact angle	Viscosity of creams	Exponential	0.979	Fig. 3	Eq. (1)
Contact angle	Slope of η–water content	Exponential	0.841	Fig. 4	Eq. (3)
Contact angle	Slope of TG-curves	Exponential	0.867	Fig. 6	Eq. (6)
Contact angle	Rate of evaporation	Exponential	0.874	Fig. 8	Eq. (8)
Contact angle	Water separation by centrifugation	Linear	0.753	Fig. 9	Eq. (9)

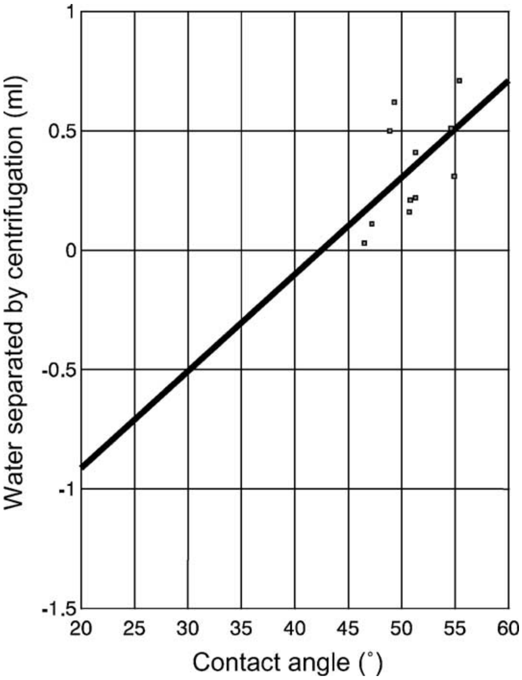

Fig. 9. The effect of wetting on the physical stability of creams containing different emulsifiers and 80% (w/w) water (11 composition).

4. Conclusion

Our experiments proved that the consistency and the stability of the investigated coherent emulsions were determined by the structure of the interface.

The following relationships were found between the quantitative parameter: the wetting contact angle and the cream characteristics:

- viscosity versus contact angle: exponential function;
- slope of concentration function versus contact angle: exponential function;
- slope of the TG-curves versus contact angle: exponential function;
- evaporation rate versus contact angle: exponential function;
- separated water after centrifuging versus contact angle: linear function.

It can be stated, based on the experiments, that the most important preformulation test in the design of cream-compositions is the quantitative determination of wetting between the hydrophilic and lipophilic phase.

Emulsifiers also can be characterized by these wetting investigations. It is essential to determine the decrease in the value of contact angle at the water and oil interface when using a new emulsifier in different concentrations.

The following methods are advised in order to exactly characterize the structure and stability of cream-systems high water content: determination of the wetting angle, rheological examinations, thermogravimetrical measurements, and their correlation with the above-mentioned experiments.

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