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SHORT COMMUNICATIONS

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Lamellar liquid crystals made of anionic surfactant, oleic acid, diethyleneglycol monoethyl ether and water

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Abstract Lamellar liquid crystal formulation, with very low surfactant content, was optimized for the system made of phosphated oleyl ether 3 mol ethylene oxide as anionic surfactant, oleic acid as hydrophobic ingredient, diethyleneglycol monoethyl ether as cosolvent and water. The appropriate relationships between surfactant, fatty acid and glycol to promote the lamellar liquid crystal structure through further water dilution, were established. The physical appearance of these liquid crystals corresponded to viscous transparent gels. The realms of existence of the gels were stated in terms of minimum–maximum percentage of water incorporated. The main goal of this research was to decrease the surfactant content (in the range of 2–5%) needed to form liquid crystals, when usually high percentages are necessary. The study was completed with the rheological behaviour and structural parameters of some of these transparent gels. The attractive aspect of the samples, the perfect transparency and compactness, as well as the similarity to the lamellar liquid crystal structure of the intercellular lipids in the stratum corneum, permit consideration of such gels as adequate topical formulations both in cosmetics and pharmaceuticals.

Keywords Lamellar liquid crystals · Transparent gels · Anionic surfactant · Oleic acid · Glycols

Introduction

The possibility of disposing of liquid crystal formulations with optical transparency and gelled appearance is highly appreciated in several fields of application such as cosmetics and pharmaceuticals [1–6]. Lamellar structures, very similar to those present in living organisms are especially interesting as delivery systems when hydrophilic or lipophilic actives are incorporated in the corresponding domains. In this investigation, a very simple system made of phosphated oleyl ether 3 EO as surfactant, oleic acid (OA) as hydrophobic ingredient, diethyleneglycol monoethyl ether (DEGEE) as cosolvent and water, was studied to establish the optimal conditions to formulate transparent gels. These gels were structurally identified as lamellar liquid crystals. In a previous study [7], a more complex system with the same components but including propylene glycol as secondary cosolvent was considered. In the present work, however, the study was focused to explore the full possibilities of this reduced system. Though it is well stated that liquid crystals can be easily prepared, its real application in certain fields such as cosmetic and pharmaceutical is seriously limited given the usual high surfactant concentrations required [8–10]. The advantage of our system lies in the very low surfactant concentration (2–5%) and in the harmlessness of the ingredients (OA is one of the main fatty acids of the human stratum corneum [11], the glycol acts as moisturing agent) allowing to predict a biological compatibility of its topical application. Moreover, from the fundamental research point of view it is interesting to analyse the ratios between the different ingredients allowing the construction of ordered structures of lamellar liquid crystals [12].

Materials and methods

Materials

Phosphated oleyl ether 3 EO (S) from Croda; OA from Fluka; DEGEE from Merck; deionized water (W).

Pseudoternary phase diagram elaboration

Partial pseudoternary phase diagrams were considered, in which one of the apex was shared by OA and DEGEE in a given [OA/DEGEE] ratio, the second apex was occupied by the surfactant (S), and the third by water (W). The experimental procedure consisted of preparing different initial samples by combinations between S and [OA/DEGEE] (basic compositions) that were further subjected to a progressive water titration. Samples were classified according to its phase behaviour and the realms of existence of the transparent monophasic liquid and gelled compositions were delimited in the corresponding diagrams.

Sample preparation

Samples of 1 g were prepared in glass tubes with a stopper by weighing the surfactant and adding the combination between OA and glycol previously prepared. Once the surfactant was dissolved in the liquid mixture, samples were subjected to a progressive water titration. After each water addition, samples were homogenized by agitation (vibromix Heildolph Reax 2000) . When viscous samples appeared, they were centrifuged (4,000 rpm for 5 min in a Heraeus Sepatech Aerofuge Ae) to facilitate their homogenization and to eliminate air bubbles. It is important to point out that the transparent gel compositions correspond to monophasic structures of liquid crystal, and consequently, in its preparation it is not necessary to furnish the high mechanical or thermal energy required for other formulations based on emulsions. The formation of the crystal liquid compositions occurred almost spontaneously when the ingredients were placed in the appropriate proportions, and only a slight agitation was required to help the mixing of the components.

Sample classification

The transparent samples were classified as monophasic fluid liquids or monophasic gels in accordance with the visual criteria of clear–turbid, and fluid–viscous. A sample was considered as a gel when it did not flow against gravity when the tube was inverted. The observation of the homogeneous transparent samples through crossed polarizing filters established the isotropy (for the liquid compositions) and the anisotropy (for the gel compositions) of the samples. Microscopic observation through polarized light (Reichert Polyvar 2) of the anisotropic gels revealed the typical pattern of a lamellar liquid crystal structure. Small angle X-ray spectroscopy (SAXS) measurements confirmed these structures and furnished the corresponding interlamellar distances (Siemens KF 760 X-ray generator, Kratky camera of small angle M. Braun, wavelength corresponding to the CuK_α line 1.542 Å, linear detector PSD-OED 50 M. Braun, and temperature controller Peltier KPR AP PAAR).

The intervals of existence of both homogeneous liquid and gel compositions were expressed in terms of minimum–maximum water percentages incorporated.

Rheological study

The rheological behaviour of some of the liquid crystal compositions were studied at 25 °C registering the shear stress/shear rate rheograms in a cone-plate viscometer (Ferranti-Shirley MK III). A cone with a diameter of 70 mm. and angle of 0.3° was used. A typical plastic behaviour was observed for most of these compositions, evidenced by the ‘‘yield value’’, the minimum shear stress necessary to promote its flow. From the registered graphs and by means of the appropriate constants of shear stress and shear rate of the cone ($K_{SS}=22.530$ and $K_{SR}=17.903$) the data of yield values and viscosities were calculated in mPa and mPa s respectively.

Results and discussion

Basic compositions made of different surfactant concentrations (from 5% to 40%) and the corresponding remaining percentages up to 100% shared by combinations of [OA/DEGEE], in ratios ranging from 1/9 to 1/1.5, were prepared to establish the necessary conditions to form transparent gel when diluted with water. In

Fig. 1, black points correspond to the compositions that furnish these gels when water is further incorporated.

It can be noticed that a certain relationship between surfactant and OA exists. For low surfactant percentages (i.e. 5%) the appropriate ratios [OA/DEGEE] (between 1/7 and1/4) indicates a low oleic acid content whereas when the surfactant percentage increases, the shift of [OA/DEGEE] ranges indicate the possibility of incorporating higher percentages of OA. Figure 2 shows the range of percentages of OA allowing the liquid crystal formation depending on the surfactant concentration.

Having once established the relationships between the ingredients allowing the further formation of the transparent gels, the next aspect to be considered is in which extension (minimum–maximum water percentage) these gels are possible. Figure 3 shows the intervals of existence in percentage water of the liquid and transparent gels as a function of the [OA/DEGEE] ratio for moderate initial surfactant concentrations (5, 10, 15 and 20%). It is important to remark that through corresponding water dilution, the resulting final surfactant concentration in the gels will be highly reduced.

Figure 4 shows the partial pseudoternary phase diagrams obtained for [OA/DEGEE] ratios 1/5, 1/4, 1/3 and 1/2 and initial surfactant concentrations in the range of 5–60%.

When comparing the diagrams, it can be seen that when the [OA/DEGEE] ratio changes from 1/5 to 1/2, the area of transparent gel increases in size as it moves progressively towards higher surfactant concentrations. Among all possible compositions and bearing in mind a possible application, those requiring the lowest surfactant concentrations are especially interesting. Table 1 shows several selected compositions.

The very low surfactant percentages of certain compositions are noticeable whereas the compactness of the samples suggests higher concentrated compositions.

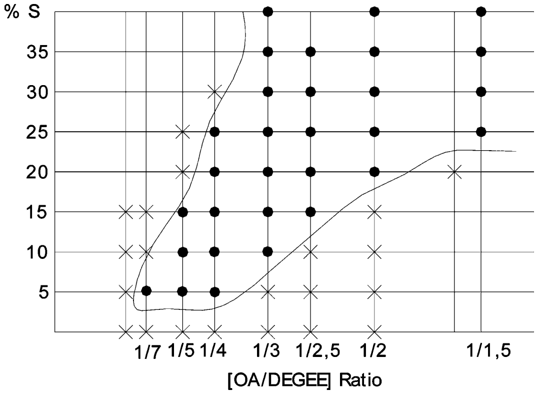

Fig. 1 Necessary conditions of the basic samples in terms of surfactant percentage and [OA/DEGEE] ratios to promote the transparent gel formation when diluted with water

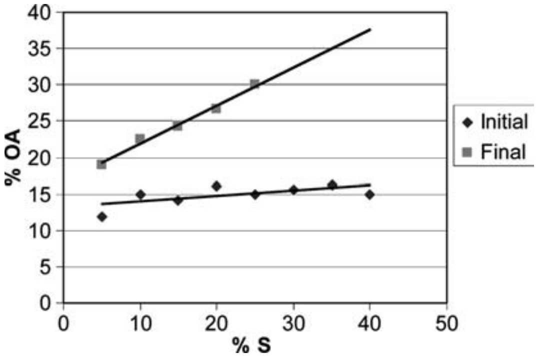

Fig. 2 Range of percentages of OA giving transparent gels depending on the surfactant concentration

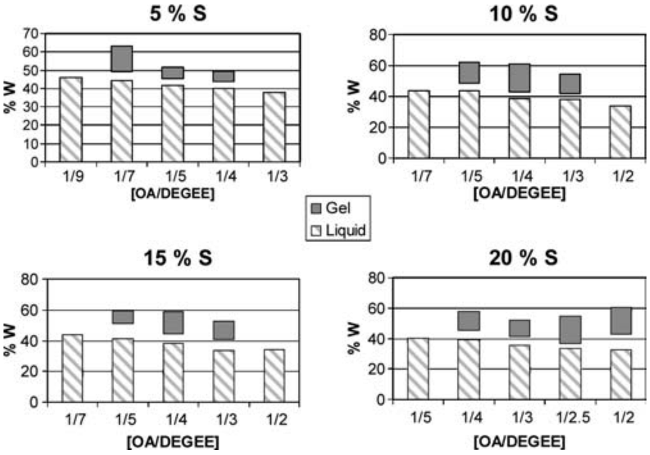

Fig. 3 Intervals of existence in percentage water of the monophasic compositions of isotropic liquid and transparent gels depending on the [OA/DEGEE] ratio and on the percentage of initial surfactant

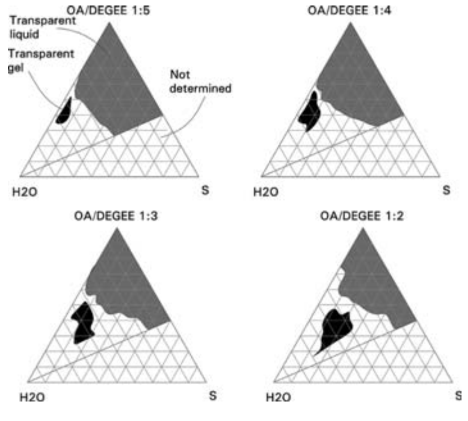

Fig. 4 Partial pseudoternary phase diagrams delimiting the realms of isotropic liquid compositions (*in grey*) and transparent gels (*in black*), depending on the [OA/DEGEE] ratio

Table 1 Transparent gels obtained from some selected basic compositions

Basic compositions (before water dilution)		Final transparent gel compositions (after water dilution)			
Ratio [OA/DEGEE]	S (%)	W (%)	S (%)	OA (%)	DEGEE (%)
1/7	5	60.0	2.0	4.8	33.2
1/5 (diagram I)	5	52.0	2.4	7.6	38.0
	10	60.0	4.0	6.0	30.0
	15	58.0	6.3	6.0	29.7
1/4 (diagram II)	5	48.0	2.6	9.9	39.5
	10	60.0	4.0	7.2	28.8
	15	56.0	6.6	7.5	29.9
1/3 (diagram III)	10	50.0	5.0	11.2	37.8
	15	50.0	7.5	10.6	31.9
	20	50.0	10.0	10.0	30.0
1/2 (diagram IV)	20	60.0	8.0	10.7	21.3
	25	60.0	10.0	10.0	20.0

Fig. 5 Typical lamellar liquid structure observed through microscopic observation under polarized light observed for these transparent gels

There is a special relevance of the role played by glycol, that after water, is the main component according to its concentration. If considering the whole of the hydrophilic components, water and glycol, they cover 80–90% of the final formulation. The microscopic observation of these anisotropic gels revealed the characteristic pattern of the lamellar liquid crystal structures (Fig. 5).

In these lamellar structures, lipophilic and hydrophilic layers alternate in parallel sheets.As a consequence, the lipophilic layer must be composed of double palisade of identical oleic alkyl chains of the surfactant and fatty acid, whereas their respective hydrophilic moieties integrate at the polar layer composed by water and the glycol. To investigate the influence of composition (level of water dilution, [OA/DEGEE] ratio, etc.) on the structural parameters of these lamellar phases, some samples were examined by X-ray diffraction. Table 2 shows the corresponding interlamellar distances d_L reflecting the extent of the structure.

At first sight, it is noticeable that the very large interlamellar distances obtained reflect the predominant percentage of polar phase in these compositions. When correlating the results with the liquid crystal composition, it can be seen that for the initial composition with 10% surfactant and fixed [OA/DEGEE] ratio 1/4, the higher the water percentage incorporated, the wider is the interlamellar distance. This fact can be understood intuitively by thinking that through water dilution, a progressive increase in the polar phase is produced in the composition. However, when considering the whole of the polar phase made of water plus glycol, it can be observed that the increasing in water is practically compensated by the decrease in glycol, so only a slight variation on the global percentages of polar phase occurs. Consequently, water appears as the main ingredient of the polar phase causing the interlamellar distance to enlarge .

On the other hand, for initial compositions having both the same surfactant concentration (10%) and level of water dilution (54%), the interlamellar distance decreases progressively when the [OA/DEGEE] ratio increases from 1/5 to 1/3. In this case, given the constant

Table 2 Interlamellar distances of the liquid crystals obtained from the X-ray diffraction spectra (SAXS) as a function of the transparent gel compositions

Initial composition		Dilution H_2O (%)	Total H_2O + DEGEE (%)	Interlamellar distance d_L (Å)
S (%)	[OA/DEGEE] ratio			
10	1/4	45	84.6	170.4
		50	86.0	196.6
		54	87.4	213.0
		60	88.8	264.4
	1/5	54	88.5	239.6
	1/4	54	87.1	213.0
	1/3	54	85.0	191.7

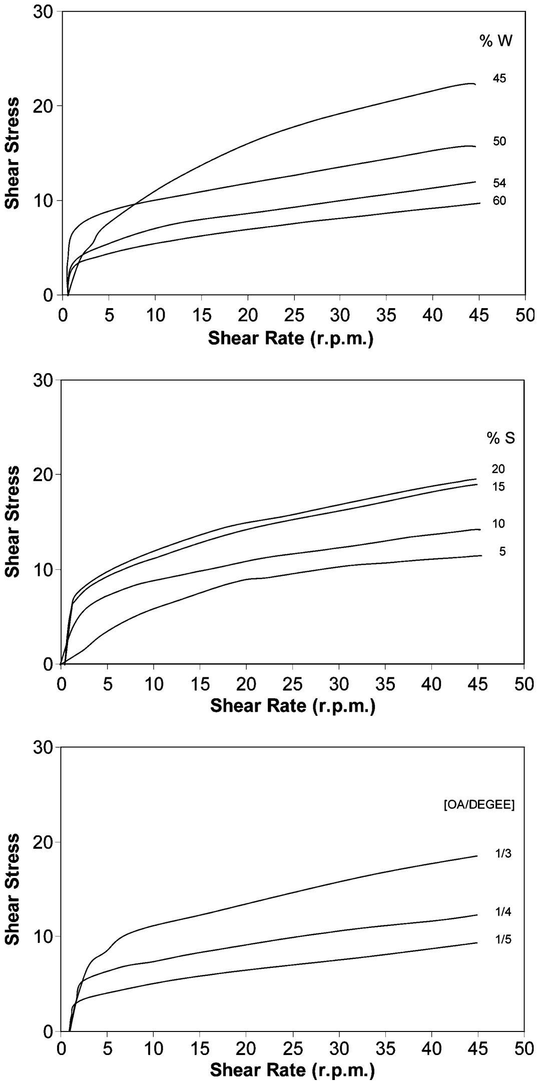

Fig. 6 Rheograms evidencing the influence of the different factors involved in the composition. **a** Influence of water dilution on the basic composition made of 10% of surfactant and [OA/DEGEE] ratio 1/4. **b** Influence of surfactant concentration on compositions with [OA/DEGEE] ratio 1/4 diluted up to water percentages located approximately in the centre of the range of existence of each gel. **c** Influence of the [OA/DEGEE] ratio on basic compositions with 10% of surfactant concentration, diluted to 54% of waters

level of water dilution and the slight variation in the whole percentages of the hydrophilic phase, the decrease in the interlamellar distance must be mainly attributed to OA increase. A probable explanation could be a tight hydrophobic interaction between the identical lipophilic oleyl chains of the surfactant and OA, resulting in a more compact lipophilic palisade.

With respect to the gel compactness, the rheological characteristics of some transparent gel compositions were studied. As previously indicated, the general behaviour of these gels correspond to plastic fluids, with yield values and viscosities covering a broad range of values, depending on the sample composition. Surfactant concentration, OA/glycol ratio and level of water dilution are factors affecting the rheological parameters. In order to elucidate the influence of each of these different factors, three series of experiments were considered in which, one of the factors was varied, whereas the others were maintained constant. Thus, in the first series, the influence of the level of water dilution for a given gel was considered. For this purpose, the basic composition made of 10% of surfactant and [OA/DEGEE] ratio 1/4 was selected due to the wide range of existence of the transparent gel (from 43.2% to 60.9% water). In the rheograms of Fig. 6a, it can be seen that at the dilution of 45% (very close to the initial dilution needed to form the gel) the sample presents pseudoplastic behaviour, indicating a less initial compactness than the samples with higher level of dilutions, where the typical plastic behaviour appears, denoted by the “yield value”, the minimum shear stress that needs to be applied to promote the flow of the sample. In Table 3 the calculated data are reported. It can be seen that the highest yield value appears at 50% of water dilution (that represent approximately the centre of the gel realm), diminishing when the dilution increases. This fact must be taken into account when comparing gels formed from different basic compositions, with different intervals of existence. In these cases, a fair comparison must consider the corresponding dilutions at the centre (approximately) of its respective realms of gel, instead of a fixed water percentage.

In the next series studied, the influence of surfactant concentration on the rheological parameters of the gels was considered. The rheograms of Fig. 6b show this

Table 3 Influence of the level of water dilution (within the range of existence of the gel) on the rheological properties of the transparent gels obtained from a same basic composition

Basic composition		Transparent gels obtained through water dilution					
S (%)	Ratio [OA/DEGEE]	Range of gel (%W)	W (%)	Yield value (mPa)	Viscosity (mPa s)		
					3 rpm	15 rpm	30 rpm
10	1/4	43.2–60.9	45	(Pseudoplastic)	1292.1	583.9	411.1
			50	77 503.2	1711.6	480.0	292.0
			54	57676.8	1174.6	349.0	221.5
			60	41452.0	923.0	278.5	176.2

Table 4 Influence of surfactant concentration on the rheological properties of a transparent gel

Basic composition		Transparent gels obtained through water dilution					
S (%)	Ratio [OA/DEGEE]	Range of gel (%W)	W (%)	Yield value (mPa)	Viscosity (mPa s)		
					3 rpm	15 rpm	30 rpm
5	1/4	43.7–49.3	45	(Pseudoplastic)	503.4	322.2	218.1
10		43.2–60.9	50	77503.2	1211.6	480.0	292.0
15		44.4–58.7	50	81108.0	1778.7	543.7	344.0
20		45.5–57.7	50	84712.8	1879.4	577.2	357.4

influence on the system with the [OA/DEGEE] ratio 1/4. In Table 4 the calculated values are reported. It seems clear that the rheological parameters increase proportionally to the surfactant concentration.

Finally, the influence of the [OA/DEGEE] ratio for basic compositions with 10% of surfactant was considered at two levels of water dilution. From the corresponding rheograms (in Fig. 6c for 54% of water dilution) the data of Table 5 were calculated.

It can be observed that when the [OA/DEGEE] ratio changes from 1/5 to1/3, the sample increases progressively its compactness as indicated by the corresponding yield values. That means that samples are more compact and viscous when the proportion of OA increases.

As a consequence of the whole rheological study, it can be concluded that according to the requirements of formulation, these parameters can be modulated to attain the desired characteristics by varying the sample composition.

In spite of the fact that this study has been focussed on the transparent gels, other transparent liquid compositions with low viscosity can be also obtained (see Fig. 3) by solubilizing OA and water together.

Conclusions

The relationships between the ingredients of the basic compositions (phosphated oleyl ether 3 EO, OA and DEGEE) were optimized in order to form transparent gels through water dilution.

According to the optimization criteria of achieving the lowest surfactant content in the gel formulations, the better basic compositions are those containing low surfactant percentages and allowing simultaneously a high level of water dilution. According to this criteria, the better basic compositions are those containing 5% of surfactant and [OA/DEGEE] ratios 1/7, 1/5 and 1/4,

Table 5 Influence of the [OA/DEGEE] ratio on the rheological properties of the transparent gel

Basic composition		Transparent gels obtained through water dilution					
S (%)	Ratio [OA/DEGEE]	Range of gel (%W)	W (%)	Yield value (mPa)	Viscosity (mPa s)		
					3 rpm	15 rpm	30 rpm
10	1/5	48.6–61.8	50	34246.0	755.1	248.3	162.8
			54	50467.2	1023.6	312.1	194.6
	1/4	43.2–60.9	50	77503.2	1711.6	480.0	292.0
			54	57676.8	1174.6	349.0	221.5
	1/3	42.2–54.6	50	79866.0	1157.8	553.7	377.6
			54	72096.1	1644.4	526.9	332.2

furnishing transparent gels in the range of 2–2.6% of surfactant, and those with 10% of surfactant and [OA/DEGEE] ratios 1/5 and 1/4, forming transparent gels with 4% of surfactant.

The lamellar liquid crystal structure of these transparent gels was demonstrated, with noticeable wide layer of hydrophilic phase made of water and glycol that represent the 80–90% of the liquid crystal structure. The large interlamellar distances determined by SAXS reflect this fact. The influence of water percentage and [OA/DEGEE] ratio on the liquid crystal structure was determined.

From the rheological point of view, the compactness of these compositions was determined by the characteristic "yield value" of the plastic fluids, indicating the minimum shear stress necessary to overcome the gel cohesion. Once this yield is surpassed, samples flow easily when a slight tangential pressure is applied. This behaviour is especially significant for cosmetic or pharmaceutical formulations of topical use that need to be extended over the skin. The influence of the different factors involved in the rheological parameters such as surfactant concentration, OA/glycol ratio and level of water dilution was determined. As a consequence, the desired rheological properties can be modulated by modifying the composition slightly .

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