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# Polyglycerol cyclic carbonate synthesis and application to preparation of surfactant molecules

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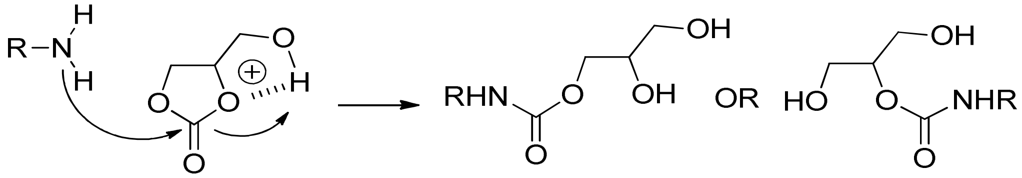
## Abstrats

In a context of sustainable development and in response to the current implementation of the REACH regulations, new surfactants are being developed from natural renewable feedstock. Their consumption forecasts will lead to a significant increase in their production. The reaction between a fatty amine and cyclic carbonates of polyglycerol offers interesting prospects in the field of surfactants. Thus, it seems possible to have very easy access to a whole range of products with amphiphilic properties which may find applications such as green surfactants.

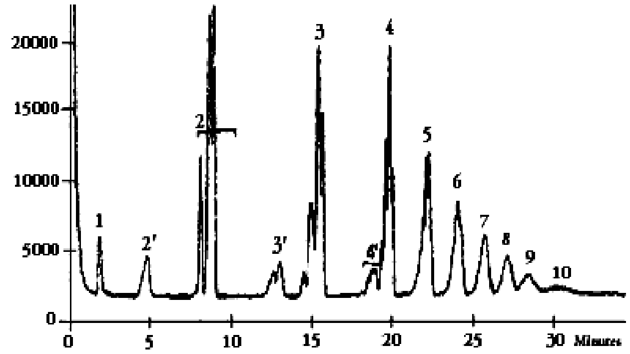
*Keywords:* glycerol carbonate, polyglycerol, surfactant naturel

## 1. Introduction

Glycerol carbonate is reported to easily react with primary amines under mild conditions ranging from ambient temperature to 50 °C [1-4]. The reaction demonstrates low regioselectivity and usually leads to a mixture of two isomers. The use of fatty amines allows one to consider obtaining products with amphiphilic surfactant properties [5-8]. The polar party engendered by glycerol carbonate is however not significant enough to confer on products obtained the desired surfactant properties.



In order to remedy these disadvantages and to obtain a greater hydrophilic part, we considered the preparation of cyclic carbonates of polyglycerol. The polyglycerol used is a PG3 provided by *NOVANCE* obtained from glycerin by polyetherification in basic medium. It is a mixture of several compounds, including of PG2, PG3, PG4, PG5, as well as PG6, PG7, PG8, PG9 and PG10 in smaller quantities. The presence of small quantities of cyclic product can also be detected [9-13] (figure 1).



1. Glycérol
2. Diglycérols
3. Triglycérols
4. Tétraglycérols
5. Pentaglycérols
6. Hexaglycérols
7. Heptaglycérols
8. Octaglycérols
9. Nonaglycérols
10. Décaglycérols

2', 3', 4' : cyclic compounds

Chromatograph VARIAN 3410 HT
Column injector - Détector FID

- phase : DB-5HT, film 0,1 µm
- column L = 15 m - Ø = 0,32 mm ID
- t°C column: 100°C → 200°C à 6°C/minute
200°C → 330°C à 12°C/minute
- t°C injector: 80°C → 330°C à 180°C/minute
- t°C détector : 350°C
- débit d'hélium 12,5 ml/minute
- make up : 25 ml/minute

**Figure 1:** GC polyglycerol PG3 column DB-5HT

Thus, on the basis of a PG3, we can write several isomers (figure 2).

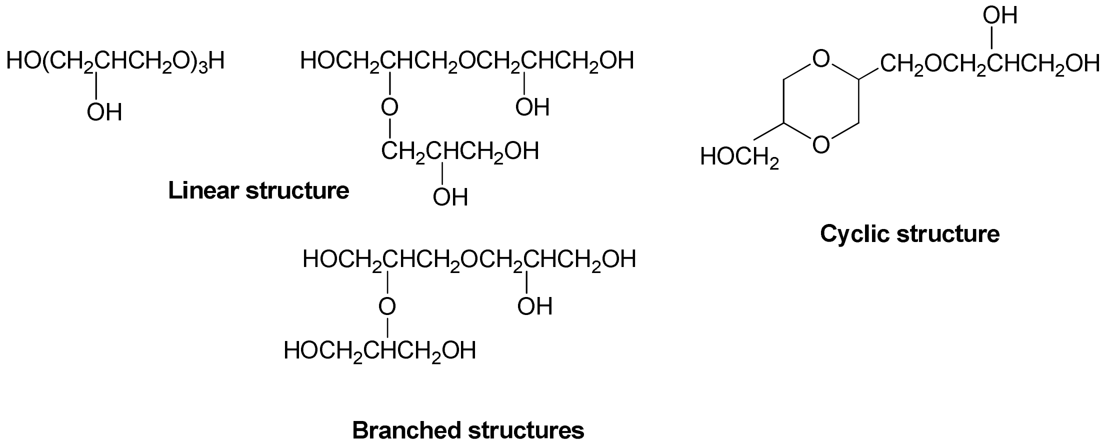


**Figure 2:** Different isomers of PG3

## 2. Materials and methods

*2.1. Materials*

Dimethyl carbonate (DMC), butylamine, dodecylamine were purchased from Fluka-Sigma-Aldrich Chimie SARL (St Quentin Fallavier, France). Polyglycerol was obtained from Novance (Compiègne, France) as a mixture of compounds with an average molecular weight of 242 (n ~ 3).

*2.2. Instruments*

$^1$H and $^{13}$C NMR spectra were recorded in water on a Bruker AM 400 spectrometer. Chemical shifts are expressed in parts per million. FTIR spectra were recorded as thin films between NaCl plates on a Perkin Elmer FTIR spectrometer SPECTRUM 2000.

*2.3. Reaction with amines*

Five membered cyclic carbonate of polyglycerol was mixed with amine at room temperature in a round bottomed flask equipped with a magnetic stirrer. Progress of the reaction was monitored by FTIR spectroscopy following the disappearance of the cyclic carbonyl band at 1780 cm$^{-1}$.

*2.4. Synthesis of carbonate PG3*

In a flask of 50 mL equipped with a refrigerant and $CaCL_2$ guard tube, we introduced 4 g (0.016 mol) PG3, a variable mass (1.5 g per equivalent) of dimethyl carbonate (DMC) and a catalytic amount 0.057 g (2.5 mmol) of $K_2CO_3$. The reaction mixture was stirred at the temperature of 70°C for 3 hours and then the methanol and the DMC in excess were distilled at reduced pressure of 0.05 mbar in glass oven at 40 °C.

**$^1$H NMR** (400 MHz, DMSO-$d_6$),  (ppm): 4.89 (m, 2H); 4.81- 4.77 (broad s, OH); 4.51 (m, 2H); 4.28 (m, 2H); 3.78-3.16 (m, polyglycerol protons)

**IR** (NaCl film): 3401 (s. OH), 2931 (n. $CH_2$), 1790 (n. OC(O)O cyclic carbonate),1403 (s. $CH_2$), 1181 (s. CH), 1054 cm$^{-1}$ (s. OH).

*2.5. Condensation of amines*

In a flask of 50 mL equipped with a refrigerant and $CaCL_2$ guard tube, we introduced 0 5eq PG3 carbonate with 1 equivalent of aliphatic primary amine solvent. The mixture was stirred for 20 min at 50 °C. The progress of the reaction was followed by IR to track the disappearance of the characteristic band for the carbonate cyclic PG3 to 1780 cm$^{-1}$ and the formation of amide a 1730 cm$^{-1}$ function.

## 3. Results and discussion

For reasons of simplification of writing, we will subsequently consider a model structure based on a linear PG3, which is obviously simplified compared to the actual product. We relied on a method for the preparation of carbonate of glycerol described in the literature [13-15], which is to catalyse the reaction using potassium carbonate from dimethyl carbonate (DMC) and glycerol. This reaction is carried out without solvent and the purification step involves distillation at 40 ° C under reduced pressure to remove the excess dimethyl carbonate and methanol formed during the reaction. We applied this method to polyglycerol of type studying in particular the influence of stoichiometry in carbonate from dimethyl (DMC) and reaction temperature on formation of cyclic carbonate selectivity acyclic /carbonate (figure 3).

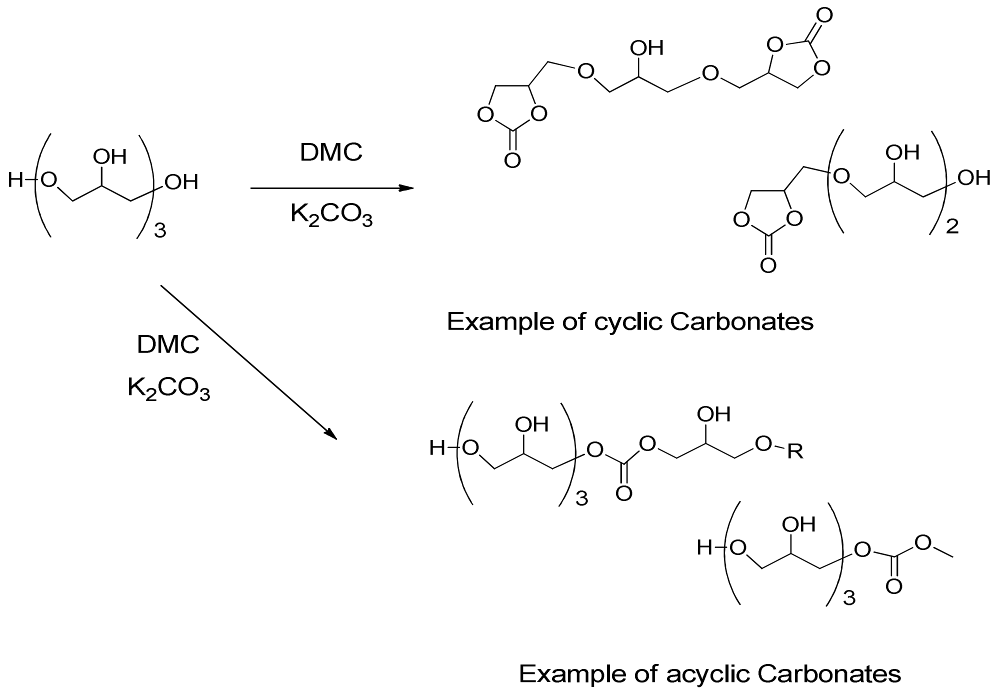


**Figure 3:** Some examples of reactions in the group of carbonate formation.

The analysis by IR, $^1$H NMR (figure 4) and $^{13}$C NMR (figure 5) of products obtained by reaction of the PG3 at 70°C with 1, 2 and 3 equivalents of DMC as well as those obtained in the thermodynamic conditions with 10 equivalents of DMC at 95 °C indicate that the reasons diols-1, 2 react first to give cyclic carbonate functions and desired cyclic compounds are obtained with 12 or 3 DMC equivalents on the basis of a PG3 for the polyglycerol.

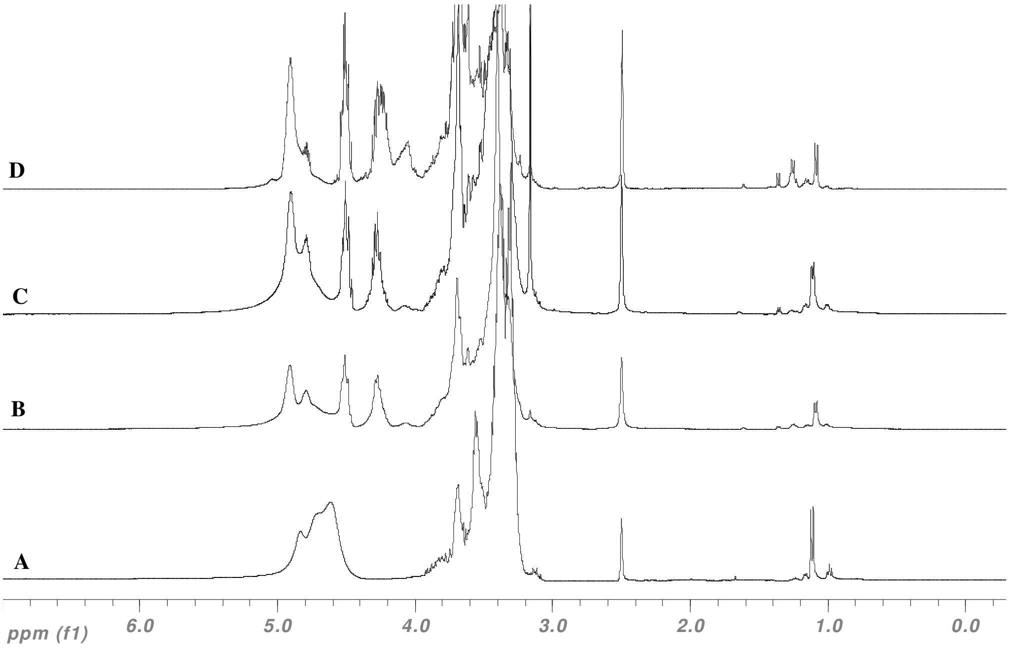


**Figure 4:** $^1$H NMR of the reaction product between PG3 and different amounts of CDM (A) PG3 (B), PG3 with 1équivalent CDM (C), PG3 with 3 equivalents of CDM, (D) with 10 equivalents of CDM.

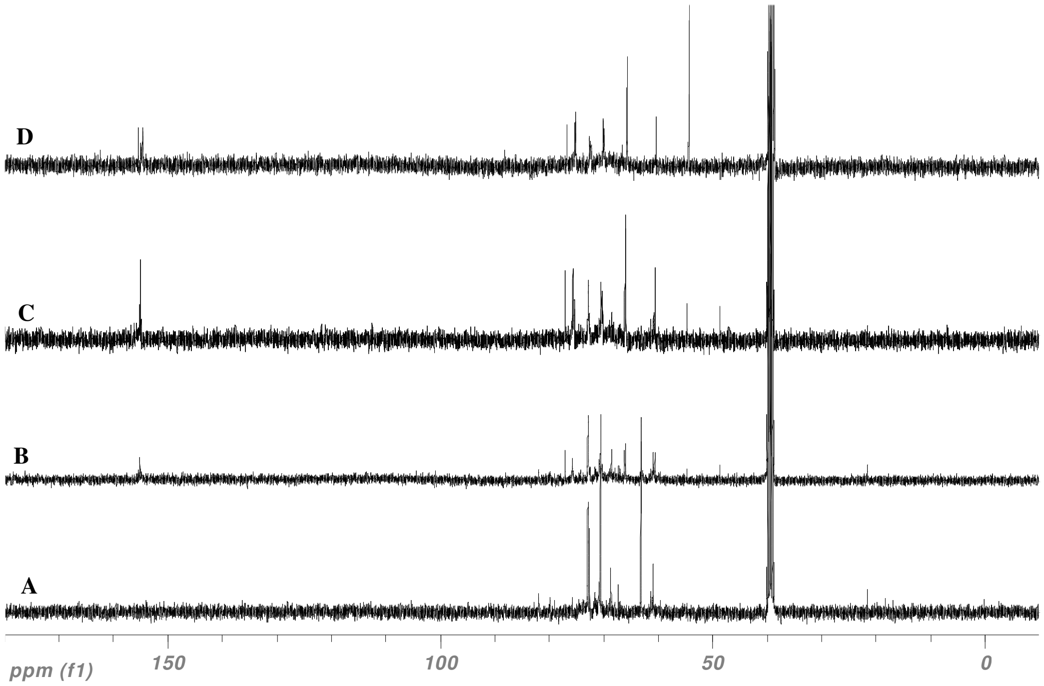
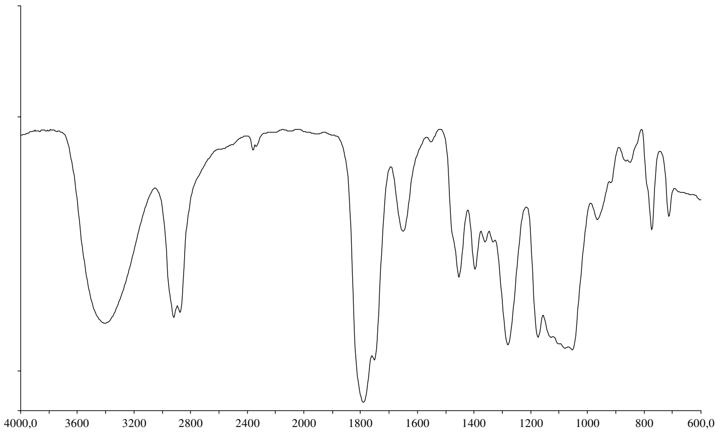


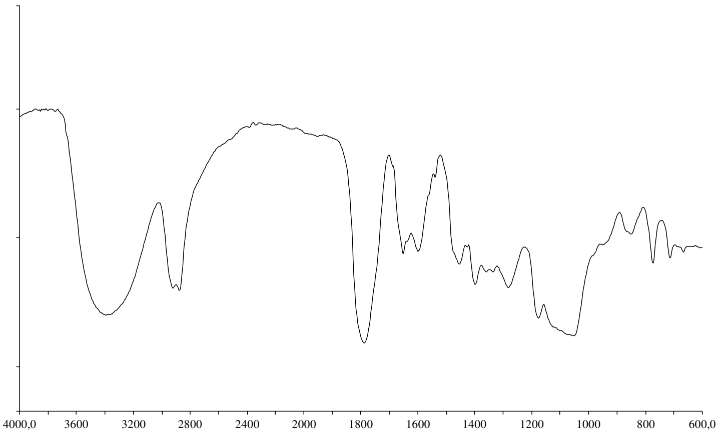
**Figure 5:** $^{13}$C NMR of the reaction product between PG3 and different amounts of CDM (A) PG3 (B), PG3 with 1équivalent CDM (C), PG3 with 3 equivalents of CDM (D), with 10 equivalents of CDM

The most flagrant proof is the appearance in IR of a band 1780 cm$^{-1}$ (figure 6) corresponds to acyclic carbonate. Similarly, signals appearing at 4.28, 4.50 and 4.90 ppm in proton NMR are characteristic of the formation of cyclic carbonate. By hardening the condition, a vibrational band appears in 1751 cm$^{1}$, indicating the formation of acyclic carbonates, probably on the hydroxyl functions remained free of the polyglycerol.

Polyglycerol + 10 equivalents of CDM



Polyglycerol + 3 equivalents of CDM



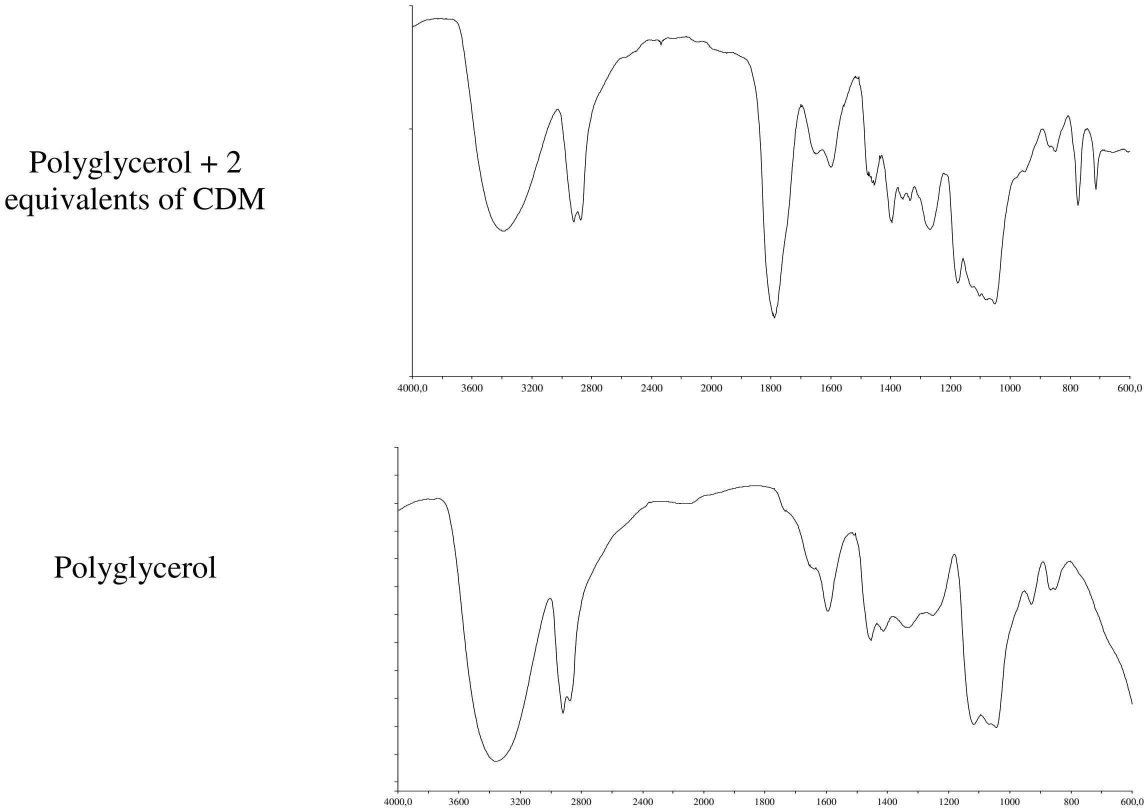


**Figure 6:** FTIR spectra of the reaction product between PG3 and different amounts of CDM

The best conditions have been obtained by refluxing in methanol during five hours a catalytic amount of potassium carbonate and three equivalents of DMC. A higher quantity of DMC was not usefull because it led to an increased ratio of non-cyclic carbonate moiety which was obviously not suitable for the following polymerization. This ratio between cyclic and not cyclic carbonate groups was also easily monitored by FT-IR experiments since the first showed a vibration band at 1780 $cm^{-1}$ while the second were detected at 1751 $cm^{-1}$. The products obtained were put in contact with different primary aliphatic amines which have reactivity similar to what had been observed for glycerol carbonate. For example, the mixture of products obtained from the condensation of the dodecylamine on PG3 cyclic carbonate obtained by reacting two equivalents of DMC for a PG3, has typical behavior of surfactant (figure 7).

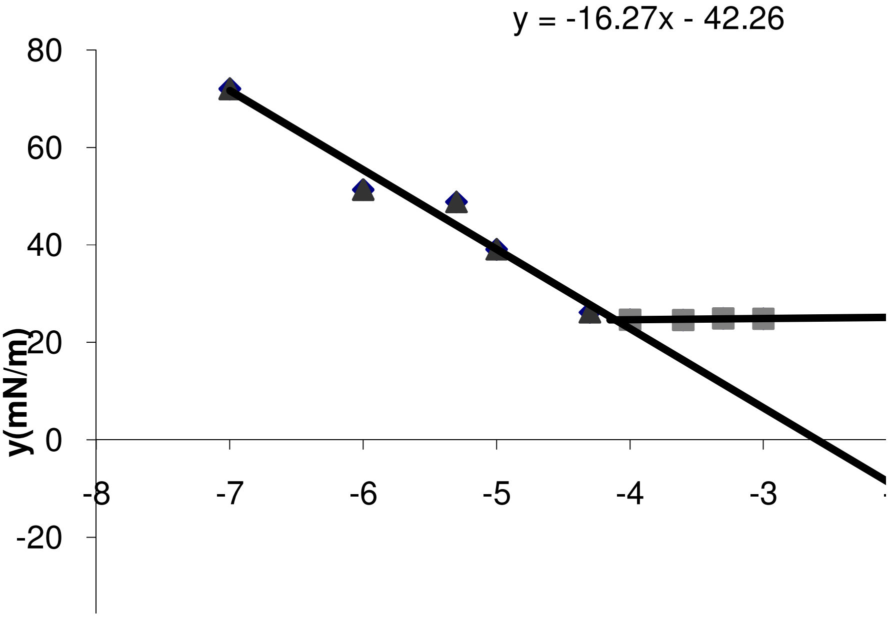


**Figure 7:** Changes in surface tension as a function of concentration

The decrease of surface tension and CMC (critical micellar concentration) value is comparable to what is generally observed for surfactants with a hydrogenated carbon chain.

## Conclusion

With the current focus on sustainable development, combined with rising of oil prices, renewable plant resources from agriculture are an attractive and potentially cost-effective alternative to petrochemical resources. The use of cyclic carbonate derived from glycerol, a renewable source material, is one such possible alternative. The mixture of products obtained from the condensation of dodecylamine on PG3 cyclic carbonate shows typical surfactants behavior; the decrease of surface tension as well as the value of CMC (critical micellar concentration) are comparable to what is generally observed in surfactants derived from petrochemicals.

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