Available online at www.sciencedirect.com
ScienceDirect
Thermochimica Acta 453 (2007) 27–30
thermochimica acta
www.elsevier.com/locate/tca

Effects of nonionic sugar surfactants on the phase transition of DPPC membranes

Bożenna Różycka-Roszak [a,*], Beata Jurczak [a], Kazimiera A. Wilk [b]

[a] *Agricultural University, Department of Physics and Biophysics, Norwida 25, 50-375 Wrocław, Poland*
[b] *Wroclaw University of Technology, Department of Chemistry, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland*

Received 25 August 2006; received in revised form 27 October 2006; accepted 30 October 2006
Available online 19 November 2006

Abstract

The influence of newly synthesized *N*-alkanoyl-*N*-methyllactitolamines (decanoyl [C_{10}MELA], lauoroyl [C_{12}MELA] and miristoyl [C_{14}MELA]) on the thermotropic phase transition of phosphatidylcholine bilayer was compared with common sugar-based surfactants *N*-dodecyl-β-D-glucopyranoside [C12G1] and decanoyl-*N*-methyl glucamide [MEGA-10]. The results indicate that C_nMELA are very active at the membrane surface and disturb the phospholipid bilayer structure less than commercially used MEGA-10 and C12G1.

Keywords: Nonionic sugar surfactants; DPPC membrane; DSC; Phase transition

1. Introduction

Sugar-based surfactants are of interest because they possess improved surface and performance properties, reduced environmental impact, and have potential pharmaceutical and biomedical applications [1–3]. These surfactants are made from renewable resources, are easily biodegradable and increasingly used in washing agents, cosmetics, and drug carriers [4,5].

N-alkanoyl-*N*-methyllactitolamines (C_nMELA) are examples of newly synthesized lactose-derived surfactants (Fig. 1). They share some performance properties (i.e., foam stabilizing and wetting with commercially available alkyl polyglucosides (Glucopon 600 EC(HH)-a Henkel product) [6]. These compounds are nontoxic to bacteria and yeasts and can be considered readily biodegradable in the Closed Bottle Test inoculated with activated sludge. The derivatives in the present study fulfil the requirements for environmental acceptance [6,7]. Due to a wide array of possible applications the interaction of C_nMELA compounds with model membranes is of interest. This paper reports the results of DSC studies.

The influence of *N*-alkanoyl-*N*-methyllactitolamines (decanoyl [C_{10}MELA], lauoroyl [C_{12}MELA], miristoyl [C_{14}MELA]) was compared on the thermotropic phase transition of phosphatidylcholine bilayer with that of commonly used sugar-based surfactants, *N*-dodecyl-β-D-glucopyranoside [C12G1] and decanoyl-*N*-methyl glucamide [MEGA-10]. To elucidate the role of the bulky head group of C_nMELA compounds, lactobionic acid [LA] was also included.

2. Materials and methods

2.1. Chemicals

1,2-Dipalmitoyl-*sn*-glycero-3-phosphatidylcholine [DPPC], *N*-dodecyl-β-D-glucopyranoside [C12G1] and decanoyl-*N*-methyl glucamide [MEGA-10] were purchased from Sigma–Aldrich, Chemie (Germany). Lactobionic acid [LA] was purchased from Fluka, Buchs (Switzerland). *N*-alkanoyl-*N*-methyllactitolamines [C_nMELA] were synthesized as described before [6].

2.2. Sample preparation for differential scanning calorimetry (DSC)

DSC studies were performed as before [8,9]. 1 mg of DPPC with appropriate amounts of the compounds, except lactabionic acid, was dissolved in chloroform. The mixtures were prepared at increasing compound/DPPC molar ratio from 0.01

* Corresponding author. Tel.: +48 71 3205249; fax: +48 71 3205172.
E-mail address: Boro@ozi.ar.wroc.pl (B. Różycka-Roszak).

0040-6031/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2006.10.027

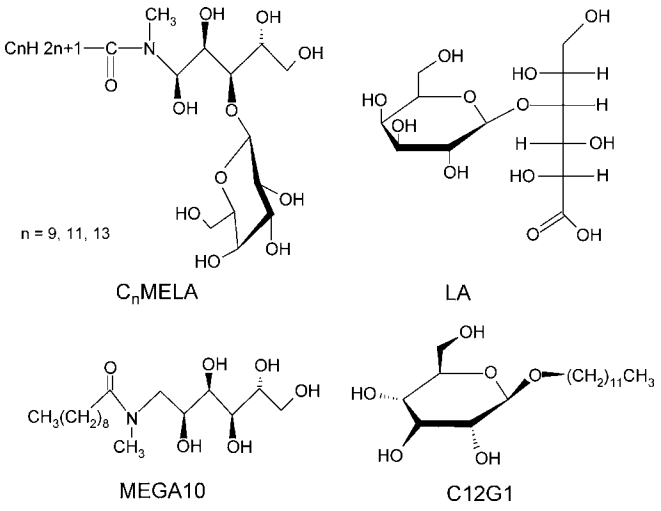

Fig. 1. Chemical structure of the compounds studied: *N*-alkanoyl-*N*-methyllactitolamines [C_nMELA], *N*-dodecyl-β-D-glucopyranoside [C12G1], decanoyl-*N*-methyl glucamide [MEGA-10], lactobionic acid [LA].

to 0.3 for LA and for sugar surfactants from 0.01 to molar ratio at which the phase transition was detected, i.e., to 0.43 for C_{10}MELA, 0.35 for C_{12}MELA, 0.3 for C_{14}MELA, 0.3 for MEGA-10 and 0.27 for C12G1. Chloroform was evaporated to form a thin mixed film on the flask wall. Distilled water was then added and the mixed film shaken at 60 °C until a milky suspension of liposomes was obtained. The final phosphatidylcholine concentration was 25 mg/cm^3. The lipid suspension was then loaded into a crucible and incubated at 4 °C for 5 days.

Due to insolubility in chloroform, the procedure was changed for lactobionic acid. As before, DPPC was dissolved in chloroform and then evaporated to form a thin film on the flask wall. The lipid film was dispersed by adding water solutions of lactobionic acid of appropriate concentration and the remaining procedure was as above.

DSC measurements were done on 34–36 mg sample with a Mettler Toledo Thermal Analysis System D.S.C. 821^e operated at heating rate of 2 °C/min from 0 to 60 °C. An empty crucible was used as reference and the temperature scale was calibrated with indium. Thermal cycles were repeated three times; the experimental error in temperature and thermal response (ΔH_m) was ±0.1 °C and ±5%, respectively.

3. Results and discussion

Thermograms were put in Supplementary data files.

3.1. Lactabionic acid (LA)

Below a molar ratio of 0.06, lactabionic acid does not affect the main phase transition temperature but abolishes the pretransition and shows a strong effect on the transition enthalpy (Figs. 2 and 3). The main transition is a little broadened but remains approximately symmetrical with increasing LA concentration. These results suggest that LA interacts with the surface of the bilayers by electrostatic interactions and hydrogen bonds.

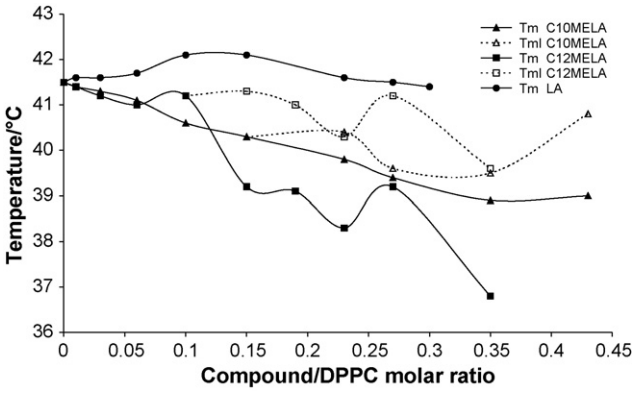

Fig. 2. The temperatures (T_m, T_m^l) of gel to liquid crystalline phase transition as a function of C_{10}MELA/DPPC, C_{12}MELA/DPPC and LA/DPPC molar ratio.

The electrostatic interactions decrease while the hydrogen bonds increase ΔH_m.

Above a molar ratio of 0.06, lactabionic acid scarcely affects the main phase transition temperature and the enthalpy. The transitions are a little broadened but remain approximately symmetrical, suggesting that, also at higher concentrations, LA interacts with the surface of the bilayer.

3.2. Sugar-based surfactants

MEGA-10 and C12G1 show similar effects to LA on DSC curves. The compounds decrease ΔH_m, abolish the pretransition and broaden the main phase transition, particularly on the low temperature side. These decrease the main phase transition temperature to a greater extent than C_{10}MELA and C_{12}MELA that have, respectively, the same chain lengths. This may be ascribed to the significantly smaller size of the MEGA-10 and C12G1 head groups, resulting in deeper insertion in the lipid bilayers.

At low molar ratios all the sugar-based surfactants do not significantly change the profiles DSC thermograms, the transitions remaining rather narrow and approximately symmetrical. With increasing concentration the pretransitions disappear, the main

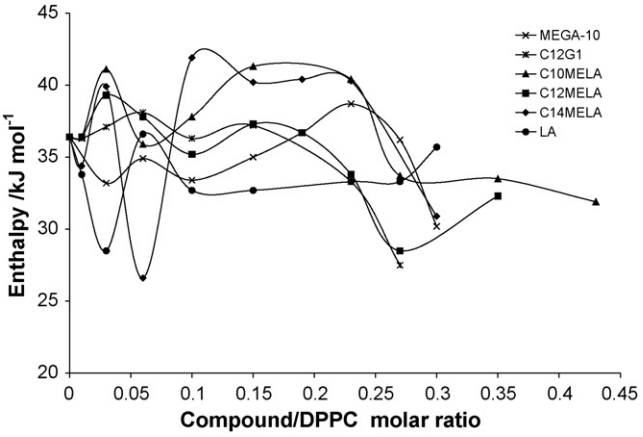

Fig. 3. The enthalpy changes of gel to crystalline phase transition as a function of MEGA-10/DPPC, C12G1/DPPC, C_{10}MELA/DPPC, C_{12}MELA/DPPC, C_{14}MELA/DPPC and LA/DPPC molar ratio.

transitions get significantly broader and asymmetrical, with visible shoulders.

The surfactant/DPPC molar ratio at which a shoulder appears (R_s) varies from one compound to another and equals 0.1, 0.06, 0.15, 0.1, 0.06 for MEGA-10, C12G1, C_{10}MELA, C_{12}MELA, C_{14}MELA, respectively. The appearance of the shoulder suggests that two peaks are superimposed and different phases coexist. Accordingly, as before [10], we analyzed the heating curves for C_nMELA/DPPC, MEGA-10/DPPC and C12G1/DPPC mixtures in the neighbourhood of the main peak by unfolding into a straight base line and two Gaussian curves fitted by least-squares. The resulting parameters, i.e., Gaussian maximum positions (T_m and T_m^I), are considered as temperature of component I (the bigger one) and component II (seen as a shoulder on DSC curve). Figs. 2 and 4 show T_m behaves in a similar way for all C_nMELA compounds, i.e., it decreases (mostly for C_{14}MELA) with increasing concentration. For C_{10}MELA and C_{12}MELA the T_m^I temperature is higher than T_m and almost independent of concentration. The T_m^I temperature behaves in a similar way for C_{10}MELA and C_{12}MELA but differently for C_{14}MELA, whose T_m^I is lower than T_m and decreases with increasing concentration. This may indicate that C_{10}MELA and C_{12}MELA induce phases in the lipid bilayer different than C_{14}MELA. According to the hypothesis by Jain and Wu [11], a compound that specifically interacts with the polar group of DPPC promotes phase separation. This suggests that C_{10}MELA and C_{12}MELA interact with the polar head groups of lecithin differently than C_{14}MELA, which is probably due to deeper location of C_nMELA in the phospholipid bilayer.

For C_{10}MELA and C_{12}MELA the temperature T_m^I is higher than T_m and is very similar to T_m of DPPC, as well as those of DPPC in the presence of LA. This similarity suggests that C_{10}MELA and C_{12}MELA may interact with the surface of the bilayer in a similar way as LA, which in turn may indicate that component II refers to domains of pure DPPC. The formation of domains of pure DPPC and domains of DPPC with C_{10}MELA or C_{12}MELA in the gel phase seems to be quite likely because of the possibly low miscibility between DPPC and C_nMELA due to their very bulky head groups.

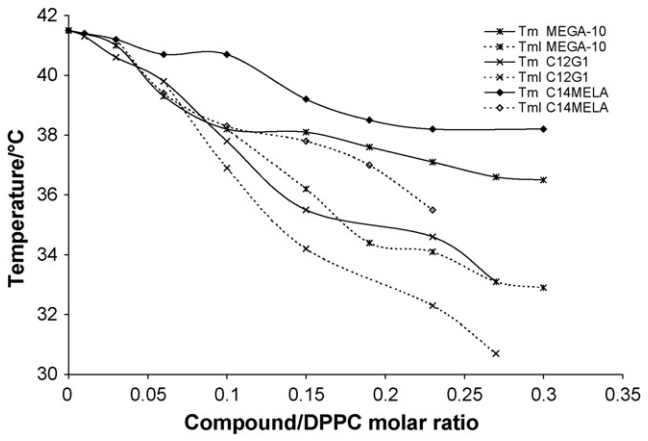

Fig. 4. The temperatures (T_m, T_m^I) of gel to liquid crystalline phase transition as a function of MEGA-10/DPPC, C12G1/DPPC and C_{14}MELA/DPPC molar ratio.

For C_{14}MELA like for MEGA-10 and C12G1 the T_m^I temperature is lower than T_m and decreases with increasing concentration (Fig. 4). This similarity suggests that C_{14}MELA interacts with the surface of the bilayer in a similar way as MEGA-10 and C12G1. This, in turn, suggests that C_{14}MELA is embedded deeper into the lipid bilayer than C_{10}MELA and C_{12}MELA. This is probably the consequence of stronger hydrophobic interactions between C_{14}MELA (due to the longest chain) and phospholipids chains than that of other C_nMELA compounds.

Below R_s the C_nMELA compounds show different effects on ΔH_m than Mega-10 and C12G1. The conventional surfactants scarcely affect ΔH_m while C_nMELA shows a strong dual effect on ΔH_m (Fig. 3). In the presence of C_nMELA the transition enthalpy first increased and then decreased. When a surfactant molecule enters into a phospholipid bilayer it disrupts the bilayer structure and decreases ΔH_m. On the other hand the hydroxyl groups of an inserted surfactant may form hydrogen bonds with the polar heads of DPPC resulting in increased ΔH_m. Thus, an increase in the overall enthalpy may indicate that surface interactions are stronger than disruptive ones. From Fig. 3, at concentrations below R_s the C_nMELA compounds increase the enthalpy to significantly greater extent than MEGA-10 and C12G1. This suggests that C_nMELA interacts with the surface of liposomes stronger than conventional surfactants.

At higher concentrations, above R_s the transitions get significantly broader, due to the disruption of the bilayer structure (decrease in cooperativity) and to the fact that the transition is a superposition of two peaks. The disruption accounts for decreased ΔH_m. The superposition probably occurs due to surface interactions [11] and accounts for increased ΔH_m. Thus, the greater overall enthalpy suggests a lower ability of a surfactant to disrupt the bilayer structure. The C_nMELA compounds increase the overall enthalpy (Fig. 3) significantly more than conventional surfactants. This suggests that also at concentrations above R_s the C_nMELA compounds are more active on the level of the membrane surface and disturb the phospholipid structure less than the conventional surfactants.

4. Conclusions

The compounds MEGA-10 and C12G1 decrease the main phase transition temperature to a greater extent than C_{10}MELA and C_{12}MELA that have, respectively, the same chain length. This means that all C_nMELA surfactants decrease T_m to a significantly lesser extents than MEGA-10 and C12G1. The phase transitions were detectable for C_{10}MEGA and C_{12}MEGA at higher concentration than it was possible for MEGA-10 and C12G1. Besides, the C_nMELA compounds cause phase separation at higher surfactant/DPPC molar ratios than the conventional surfactants with the same chain length, i.e., 0.1 and 0.15 for MEGA-10 and C_{10}MELA, respectively, and 0.06 and 0.1 for C12G1 and C_{12}MELA, respectively. Below and above R_s the C_nMELA compounds induce greater increase in ΔH_m than the conventional surfactants used. The results suggest that all the newly synthesized C_nMELA surfactants are very active at the membrane surface, but disturb the phospholipid bilayer less than the commercially used MEGA-10 and C12G1.

Acknowledgment

The use of a DSC in the Institute of Agricultural Engineering of Wrocław Agricultural University is gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2006.01.027.

References

[1] D. Balzer, Tenside Surfact. Detergent 28 (1991) 419–427.
[2] M. Claesson, U.R.M. Kjellin, Sugar surfactants, in: Encyclopaedia of Surface and Colloid Science, Marcel Dekker, New York, 2002, pp. 4909–4925.
[3] W. von Rybiński, K. Hill, Angew. Chem. Int. Ed. Engl. 37 (1998) 1329–1345.
[4] K. Hill, O. Rhode, Fett-Lipid 101 (1999) 25–33.
[5] S. Matsumura, K. Imal, S. Yoshikawa, K. Kawada, T. Uchibiori, J. Am. Oil Chem. Soc. 67 (1990) 996–1001.
[6] K.A. Wilk, L. Syper, B. Burczyk, I. Maliszewska, M. Jon, B.W. Domagalska, J. Surfact. Detergent 4 (2001) 155–161.
[7] C.J. Drummond, D. Wells, Colloids Surf. A 141 (1998) 131–142.
[8] B. Różycka-Roszak, A. Przyczyna, Chem. Phys. Lipids 123 (2003) 209–221.
[9] B. Różycka-Roszak, A. Przyczyna, A. Pernak, Biophys. Chem. 109 (2004) 271–279.
[10] B. Różycka-Roszak, A. Przyczyna, P. Misiak, H. Pruchnik, Z. Naturforch. 61c (2006) 208–302.
[11] M.K. Jain, N.M. Wu, J. Membr. Biol. 34 (1977) 157–201.