SYNTHESIS AND SELF-ASSEMBLY STUDIES OF GLYCOSIDE SURFACTANTS AND CHROMONICS

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SYNTHESIS AND SELF-ASSEMBLY STUDIES OF GLYCOSIDE SURFACTANTS AND CHROMONICS

Field of Study: **Organic Chemistry Including Liquid Crystal and Nanotechnology**

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Abstract

This thesis focused on the synthesis and self assembly studies of compounds involving carbohydrates. Two different types of materials were studied, *i.e.* surfactants and chromonics. Physical investigations of the compounds were conducted by TGA, DSC, OPM, UV-Vis spectroscopy, ^{1}H NMR and surface tension measurements. Sugar-based surfactants are interesting compounds for pharmaceutical and personal care products. Current commercially available surfactants such as alkyl poly glucoside surfactants (APGs) are prepared from low miscibility of sugars and fatty alcohols. In order to solve the miscibility problems of the starting materials, homogenizers are required. This, however, leads to impurities in products, which affects the use of the surfactant for life science applications. Therefore, this work focused on an economic preparation of pure glycoside surfactants. The synthesis approach applied a separation of glycosides and a coupling of sugar and fatty alcohols with different length and chain branching by click chemistry. Twenty one alkyl triazole glycoside surfactants (ATGs) were prepared with more than 80% yield. Twelve of these were anomeric pure products (>95% purity) and nine were technical products of α/β anomeric mixtures. The materials were characterized for their liquid crystal behaviours. Contact penetration studies showed a whole range of lyotropic phases from lamellar to cubic and hexagonal. ATGs' CMCs were found to be lower than those of APG surfactants. An increase in their chain length meant a decrease in CMC values. Hence these materials could be identified for oil-based surfactants applications.

Chromonics or lyotropic chromonic liquid crystals (LCLCs) are formed by the self-association of aromatic disk-shaped molecules with hydrophilic groups at the periphery in aqueous solutions. The chromonics are assembled from π-π interactions of the aromatic cores. This leads to aggregates based on stacking of the molecules. Most chromonic molecules are based on ionic structures. The research embraced the synthesis and assembly studies of non ionic chromonics consisting of triphenylene-based units surrounded by glycosides. The key point for the synthesis of triphenylene core was oxidative trimerization of veratrole and guaiacol under anhydrous conditions in the presence of ferric chloride. A symmetric compound with six sugars and an asymmetric one with three sugar units were synthesized. The materials were of purity over 95% and more than 75% yield. Due to the anisotropic effect on the aromatic ring on ^{1}H NMR, the chemical shift on the aromatic ring changed when the concentration was increased. This means the materials formed aggregation and enabled the determination of critical aggregation concentrations (CAC). Moreover, this property also showed temperature dependency. At higher concentrations and under examination by polarizing light microscopy, the chromonic exhibited liquid crystalline properties (Col phase).

Abstrak

Tesis ini memberi fokus terhadap kajian sintesis dan penyusunan diri yang melibatkan sebatian karbohidrat. Dua jenis bahan telah dikaji, iaitu surfaktan dan kromonik. Kajian fizikal sebatian telah dijalankan menggunakan TGA, DSC, OPM, spektroskopi UV-Vis, ^{1}H NMR dan pengukuran ketegangan permukaan. Surfaktan berasaskan gula merupakan sebatian yang menarik untuk dijadikan produk farmaseutikal dan penjagaan peribadi. Surfaktan komersial semasa seperti surfaktan alkil poli glukosida (APGs) telah disediakan daripada gula dan alkohol lemak yang rendah kebolehcampuran. *Homogenizers* diperlukan untuk menangani masalah kebolehcampuran bahan permulaan. Walau bagaimanapun, hal ini telah menyumbang kepada bendasing di dalam produk dan seterusnya memberi kesan terhadap penggunaan surfaktan bagi aplikasi sains hayat. Kerja ini tertumpu kepada penghasilan surfaktan glikosida tulen secara ekonomi. Pendekatan sintesis melibatkan pemisahan glikosida dan padanan gula serta alkohol lemak dengan pelbagai kepanjangan dan rantaian cabang melalui kimia klik. Sebanyak 21 surfaktan alkil triazole glikosida (ATGs) telah disediakan dengan peratusan hasil melebihi 80%. Dua belas daripadanya merupakan produk anomer tulen (>95%) dan sembilan yang lain adalah produk teknikal yang terdiri daripada campuran anomer α/β. Sifat hablur cecair bahan-bahan ini telah dikaji. Kajian 'contact penetration' telah menunjukkan kepelbagaian fasa liotropik dari lamelar kepada kubik dan heksagon. Kepekatan kritikal miselar (CMC) bagi ATG adalah lebih rendah daripada surfaktan APG. Peningkatan panjang rantaian mereka, mengurangkan nilai CMC. Oleh itu, bahan ini berkemungkinan boleh digunakan untuk aplikasi surfaktan berasaskan minyak.

Kromonik atau hablur cecair kromonik liotropik (LCLCs) terbentuk dari penyatuan diri molekul-molekul berbentuk cakera aromatik dengan kumpulan hidrofilik di pinggir larutan akueus. Kromonik ini menyusun disebabkan oleh interaksi π-π teras aromatik. Ini membawa kepada pengagregatan berdasarkan kepada penyusunan molekul. Kebanyakan molekul kromonik berdasarkan struktur ionik. Penyelidikan ini melibatkan kajian sintesis dan penyusunan diri kromonik bukan-ionik yang terdiri daripada unit berasaskan triphenylene yang dikelilingi oleh glikosida. Tumpuan utama bagi sintesis teras triphenylene adalah oksidatif *trimerization veratrole* dan guaiacol di bawah keadaan yang kontang dengan kehadiran ferik klorida. Satu sebatian simetri dengan enam unit gula dan satu sebatian tidak-simetri dengan tiga unit gula telah disintesis. Bahan-bahan ini telah dihasilkan dengan ketulenan yang tinggi melebih 95% dan peratusan hasil lebih daripada 75%. Disebabkan oleh kesan tidak-isotropik pada gelang aromatik dalam ^{1}H NMR, anjakan kimia pada gelang aromatik telah berubah dengan peningkatan kepekatan. Ini bermakna, bahan-bahan telah membentuk pengagregatan dan membolehkan penentuan kepekatan kritikal pengagregatan (CAC). Tambahan pula, sifat ini juga menunjukkan kebergantungan terhadap suhu. Pada kepekatan yang lebih tinggi dan pemerhatian di bawah mikroskop polarisasi cahaya, kromonik ini menunjukkan sifat hablur cecair (fasa Kol).

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List of Abbreviations

2-D	2-dimensional (NMR)
Ac	Acetyl
Ac_2O	Acetic anhydride
APG	Alkylpolyglucoside
Ar	Aryl
ATG	Alkyl triazole glycoside
$BF_3.Et_2O$	Boron trifluoride diethyl etherate
br	(NMR) broad signal
CD_3OD	Methanol-d_4
$CDCl_3$	Chloroform-d
CH_2	Methylene
CH_3	Methyl group
CMC	Critical micelle concentration
Col	Columnar
Cr	Crystals
Cub, Q	Cubic
d	(NMR) doublet
D_2O	Deuterium oxide
DCM	Dichloromethane
dd	(NMR) doublet of a doublet (double doublet)
ddd	(NMR) double of doublet of doublet
DEPT	Distortionless Enhancement by Polarization Transfer
DFT	Density Functional Theory
DMF	N, N-dimethylformamide
DMSO	Dimethyl Sulfoxide
DMSO-d_6	Dimethyl sulfoxide-d6
DSC	Differential scanning calorimetry
e.g.	for example
EDTA	Ethylenediaminetetraacetic acid
et al.	and others
etc.	and the others
EtOAc	Ethyl acetate
EtOH	Ethanol
Glc	Glucose
h	hour(s)
H_1	Normal hexagonal
HMQC	C-H Correlation Spectroscopy
HPLC	high performance liquid chromatography
I	Isotropic
IR	Infra-Red spectroscopy
IUPAC	International Union Pure and Applied Chemistry
J	coupling constant
LAS	linear alkyl benzene sulfonates
LC	Liquid crystal

LCLC	Lyotropic chromonic liquic crystal
L_α	Lamellar phase
M	(NMR) multiplet
m_c	Multiplet center
Me	Methyl
MeOH	Methanol
min	Minute(s)
N_2	Nitrogen gas
NaOAc	Sodium acetate
NaOMe	Sodium methoxide
NMR	Nuclear Magnetic Resonance
Nu	Nucleophile
OPM	Optical Polarizing Microscope
POE	Polyethoxyethylene
p-TsOH	para-Toluenesulfonic acid
Py	Pyridine
ROH	Alcohol
Rt	Room temperature
s	singlet
$SnCl_4$	Tin tetrachloride
T	(NMR) triplet
THF	Tetrahydrofuran
T_K	Krafft temperature
TLC	thin layer chromatography
TP	Triphenylene core
Ts	Toluenesulfonyl
Γ	Surface tension