Synthesis and Properties of Some Novel Nonionic Polyol Surfactants

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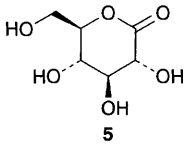
A homologous series of nonionic surfactants **4** based on sugar lactones has been synthesised and evaluated.

Over the past few years there has been increasing interest in nonionic surfactants with hydrophilic groups derived from carbohydrates. In particular, the so-called alkylpolyglucosides are being developed as commodity surfactants derived from renewable resources.[1] Many applications, for example in the biological and medical fields, require a higher degree of purity than is usually available from most commodity surfactants.† In addition, it is valuable to have homologous series of high purity compounds where the HLB (hydrophilic lipophilic balance) can be varied easily in order to understand the effects of structure on activity. This communication describes the synthesis of a novel class of nonionic surfactants, derived from the readily available carbohydrate lactones, such as δ-gluconolactone **5**, together with details of their surface activity.[2]

Alkyl gluconamides have been known for some time, and indeed they are also being developed as commodity surfactants.[3] Their use in applications at ambient temperature, or slightly above, is limited by their Krafft temperatures, which, in some cases, can be greater than 100 °C. Recent patent literature describes one way around this problem, namely sulfation.[4] However, this brings with it the penalty of making the molecule ionic. In order to develop a novel range of efficient nonionic surfactants capable of use in aqueous solution at ambient temperature, the dialkylbisglyconamides **4** were prepared (Scheme 1).

The primary goal of this approach was to design a synthesis which would allow an homologous range of alkyl groups to be incorporated in the molecules. Thus malononitrile **1** was alkylated *via* the sodium salt to give the dialkyldinitrile **2**. Attempts to stop the reaction at the monoalkylated intermediate proved difficult, but dialkylation was achieved in high yields (80–95%). Reduction of **2** was achieved using lithium aluminium hydride in diethyl ether giving diamine **3**. On a larger scale this was unacceptable and lithium in a liquid ammonia–ethanol mixture was used. Catalytic hydrogenation failed to give **3** with any of a wide range of catalysts and conditions. This was presumably due to intramolecular reaction of an amine with an unreduced nitrile group. No product was isolated even using acetic anhydride to trap out the amine as it formed.

The final step involved reaction of the diamine with the sugar lactone, such as δ-gluconolactone **5**, which was readily accomplished in refluxing methanol. The products **4** were isolated by evaporation of the solvent followed by recrystallization, usually in ethanol or acetone.



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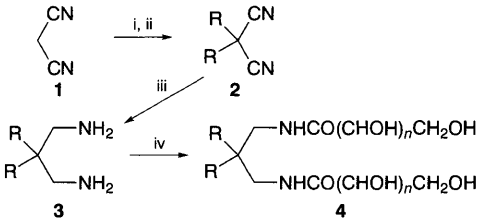

Scheme 1 *Reagents and conditions*: i, NaOEt, EtOH; ii, RBr, 80–95%; iii, $LiAlH_4$, Et_2O, 75–90%; iv, MeOH, sugar lactone, 90–95%

The compounds **4** were evaluated for their efficiency as surfactants by measuring their equilibrium surface tensions as a function of log concentration, some of which are shown in Fig. 1. Critical micelle concentrations and minimum surface tensions were estimated from the surface tension curves. Areas per molecule, at the air–water interface, were calculated from the maximum slope of the curves using the Gibbs adsorption equation.

The compounds prepared and their associated physical data are shown in Table 1.

What becomes clear from this data is that the choice of sugar lactone has much less effect on the surface properties of these compounds than varying the hydrophobic chain length. Changing the alkyl chain length by one carbon changes the CMC by an order of magnitude, whereas increasing the number of hydroxy groups on the sugar lactone by one increases the CMC by a factor of < 2.5.

Compound **4a** is extremely water-soluble and does not reach its CMC at any useful concentration (Fig. 1). Compound **4g**, in contrast, has a very low CMC and limited water solubility. More hydrophobic compounds have been made with R = C_9H_{19}–$C_{18}H_{37}$, all of which have minimal water solubility. However, the longer chain materials do exhibit lipid-like properties when sonicated in water, such as vesicle formation.

Of the water-soluble compounds, only **4e** and **4f** show Krafft temperatures, the heptonamide **4f** possessing a lower value than the gluconamide **4e**. Surprisingly, the diheptyl compound **4e** is more crystalline than its more hydrophobic dioctyl homologue **4g**.

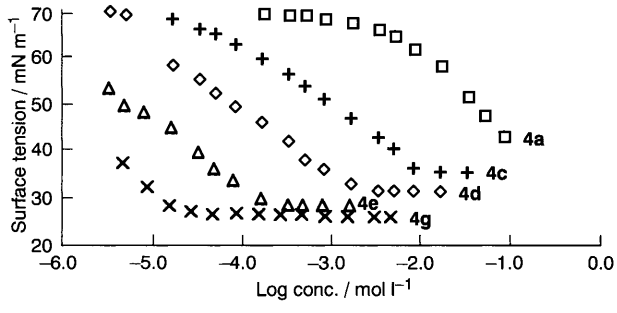

Fig. 1

Table 1 Physical properties of compounds **4**

4	R	*n*	RMM	CMC (wt%)	ST Minimum	Area mol^{-1} /± 4 $Å^2$	Krafft *T*/°C
a	C_4H_9	4	542	—	—	—	—
b	C_5H_{11}	3	510	0.2871	—	66	—
c	C_5H_{11}	4	570	0.7000	35.7	72	—
d	C_6H_{13}	4	598	0.1530	31.7	79	—
e	C_7H_{15}	4	626	0.0124	28.5	69	34.5
f	C_7H_{15}	5	686	0.0173	—	76	29.0
g	C_8H_{17}	4	654	0.0012	26.5	—	—

For homologous straight chain surfactants there is a general relationship between the CMC and the number of carbon atoms in the hydrophobic chain,[5] eqn (1).

$$\log \text{CMC} = \text{A} - \text{BN} \quad (1)$$

where A is a constant for a given hydrophilic group at a given temperature and B is a constant which is particularly dependent on the surfactant type and N is the number of carbons in the hydrophobic chain. A and B reflect the respective free energy change involved in transferring the hydrophilic group and a methylene unit of the hydrophobic group from an aqueous environment to the micelle.

Using this relationship for the homologous series of gluconamides, a value of 0.47‡ was obtained for B. This is a typical value for a nonionic surfactant.[5] The value of A was 2.32.‡

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Footnotes

† *e.g.* 1-*O*-Octyl-β-D-glucopyranoside, available from Aldrich Chemical Co.

‡ Goodness of fit, $R^2 = 0.986$.

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