Electrochemical behaviour of new electroreducible amphiphilic saccharide derivatives II: Electroreduction in protic media†

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The electrochemical reduction of new amphiphilic molecules derived from sugars and aromatic ketones has been performed in protic media under basic and acidic conditions. Exhaustive electrolyses have yielded, regardless of pH, the alcohol resulting from two-electron and two-proton exchanges. No trace of pinacol was detected. This unusual behaviour has been related to the properties of the saccharidic moiety, which can favour a highly hindered bent back conformation. The dimerisation reaction is thus less probable. Molecular calculations and a dynamic study in aqueous solution have shown that the less energetic conformations are stabilised by hydrogen bonds between the sugar moiety and the carbonyl group by means of six water molecules, three of them building a solvation chain between the carbonyl function and the primary alcohol of the sugar. As a comparison the same calculations, applied to an aprotic solvent (DMF), indicate an extended form for the conformation of lowest energy.

Réduction électrochimique de nouvelles molécules amphiphiles dérivées de sucres. Partie II : Etude en milieu protique.
En milieu protique, la réduction électrochimique de nouvelles molécules amphiphiles dérivées de sucres et de cétones aromatiques a été réalisée en milieu basique et acide. Les électrolyses exhaustives ont permis d'isoler, quel que soit le pH, l'alcool résultant du transfert de deux électrons et de deux protons. Aucune trace de pinacols n'a été décelée. Ce comportement inhabituel a été relié aux propriétés du sucre présent dans la molécule. L'établissement de liaisons hydrogène avec la fonction carbonyle par l'intermédiaire de molécules d'eau entraîne une conformation globulaire très encombrée qui peut défavoriser la réaction de dimérisation. Des calculs de dynamique moléculaire ont montré que les conformations de plus faible énergie correspondent à une forme repliée faisant intervenir six molécules d'eau dont trois constituent une chaîne de solvatation maintenant l'ensemble par liaisons hydrogène. Dans un solvant aprotique (DMF), les mêmes calculs conduisent à une forme déployée pour la molécule amphiphile.

During the past decade we have studied the electrochemical behaviour of synthesised electroreducible surfactants, showing the role played by adsorption and micellisation phenomena in the partitioning and the stereochemistry of the electrochemically generated reaction products.[1–4] In this context, we have synthesised new alkylglycosides bearing an aromatic ketone as an electrochemical probe (see Scheme 1)[5,6]

Our final aim was to convert electrochemically the prochiral carbonyl group into the corresponding two-chain pinacols (**D**, radical–radical coupling) or single-chain alcohol (**M**, two-electron reduction process) in order to generate new stereogenic centres that may cause an interesting change of the surfactant properties. In a previous paper, we have described the electrochemical behaviour of these surfactant molecules and their adsorption mode at the Hg–electrolyte solution interface.[5] We have recently presented the results of macroscale electrolyses in an aprotic medium of ketones derived from D-glucose (GluAcO3, GluAcO8) and D-glucurone (LacAcO8).[6] In the present paper, we discuss the results of macroscale electrolyses of this type of compounds, performed in protic media, hydroalcoholic and aqueous solu-

tions at pH 3 and pH 9, with the help of molecular dynamics calculation.

Experimental

Syntheses

The syntheses of the all ketones have been described in previous papers.[5–7] 1-*O*-Dodecyl β-D-maltopyranoside (DOM) was purchased from Aldrich.

Samples of alcohols **M1** and **M2** were obtained by chemical reduction with NaBH$_4$ in ethanol of ketones **K1** and **K2**, respectively. A sample of alcohol **M4**, corresponding to the electrolysis of the ketone **K4**, has been isolated and characterised by ^{1}H NMR and MS (ES). The alcohol **M5** and pinacol **D5** have been obtained by chemical reduction with NaBH$_4$ and by electrolysis in DMF,[6] respectively, of 4-hexyloxyacetophenone HeAc (**K5**).

Alcohol M1. In a round bottom flask equipped with a magnetic stirring bar were introduced 60 mL of ethanol (absolute). Ketone **K1** (50 mg, 0.14 mmol, 1 equiv.) and NaBH$_4$ (8 mg, 0.21 mmol, 1.5 equiv.) were successively added. The reaction was controlled by thin layer chromatography [eluent: ethyl acetate–methanol (7 : 3 v/v); R_f (**K1**) = 0.57; R_f (**M1**) = 0.55]. After 12 h stirring at 20 °C, water (5 mL) was added then the solvents were evaporated under reduced pressure. The crude product was purified by chromatography on a silica gel

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† Part I. See reference 5.
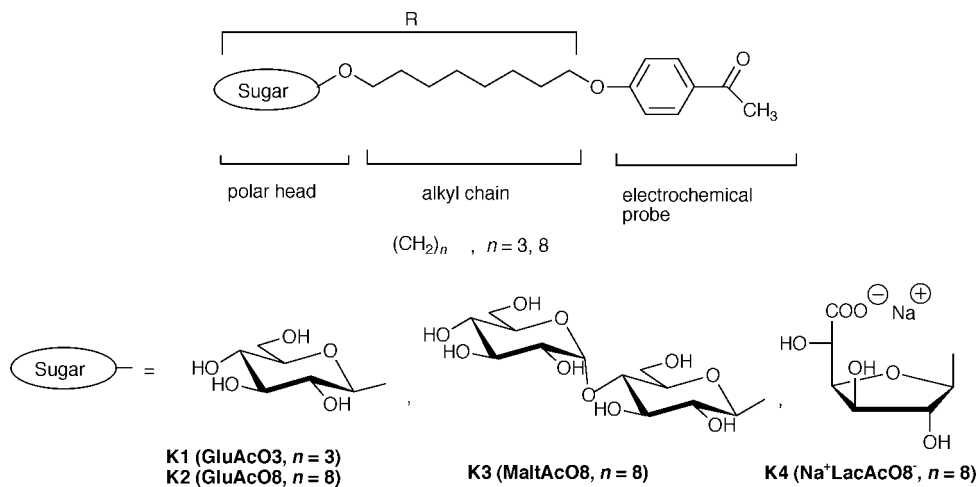
Scheme 1

column [eluent: ethyl acetate–methanol (4 : 1 v/v)]. Alcohol **M1** was obtained as a white sticky powder in 80% yield (40 mg). HRMS (FAB +): calcd $[C_{17}H_{26}O_8Na]^+$ 381.1525, found 381.1515. $[\alpha]_D^{25} = -18.1$ ($c = 1.05$, DMSO). NMR ^{1}H (400 MHz, DMSO-d$_6$): δ 7.27 (d, 2H, J 8.4 Hz, arom), 6.90 (d, 2H, J 8.9 Hz, arom), 5.06 (d, 1H, J 5.9 Hz, OH), 5.05 (d, 1H, J 4.4 Hz, OH), 4.98 (d, 1H, J 4.4 Hz, OH), 4.95 (d, 1H, J 4.9 Hz, OH), 4.69 (m, 1H), 4.53 (t, 1H, J 5.9 Hz, OH), 4.17 (d, 1H, J 7.9 Hz, H$_1$), 4.08 (t, 2H, J 6.4 Hz, CH$_2$OAr), 3.94 (m, 1H), 3.70 (ddd, 1H, J 11.8, 5.9, 2.0 Hz), 3.64 (m, 1H), 3.47 (m, 1H), 3.03–3.22 (m, 3H), 2.98 (m, 1H), 2.00 (quint, 2H, J 6.7 Hz, CH$_2$), 1.32 (d, 3H, J 6.4 Hz, CH$_3$).

Alcohol M2. The alcohol **M2** was synthesised according to the same procedure. TLC/eluent: ethyl acetate–methanol (7 : 3 v/v); R_f (**K2**) = 0.60; R_f (**M2**) = 0.58. Chromatography eluent: ethyl acetate–methanol (7 : 3 v/v). Compound **M2** was obtained as a white powder in 85% yield. HRMS (FAB+): calcd $[C_{22}H_{36}O_8Na]^+$ 451.2307, found 451.2285. $[\alpha]_D^{25} = -20.1$ ($c = 0.97$, DMSO). NMR ^{1}H (400 MHz, DMSO-d$_6$): δ 7.26 (d, 2H, J 8.4 Hz, arom), 6.90 (d, 2H, J 8.9 Hz, arom), 5.07 (d, 1H, J 3.9 Hz, OH), 5.02 (d, 1H, J 4.9 Hz, OH), 5.01 (d, 1H, J 3.9 Hz, OH), 4.97 (d, 1H, J 4.4 Hz, OH), 4.68 (m, 1H), 4.54 (t, 1H, J 5.9 Hz, OH), 4.12 (d, 1H, J 7.9 Hz, H$_1$), 3.95 (t, 2H, J 6.4 Hz, CH$_2$OAr), 3.79 (m, 1H), 3.69 (ddd, 1H, J 11.8, 5.4, 1.5 Hz), 3.37–3.50 (m, 2H), 3.01–3.19 (m, 3H), 2.96 (m, 1H), 1.72 (quint, 2H, J 7.4 Hz, CH$_2$), 1.55 (m, 2H, CH$_2$), 1.25–1.48 (m, 8H, CH$_2$), 1.31 (d, 3H, J 6.4 Hz, CH$_3$). NMR ^{13}C (100 MHz, DMSO-d$_6$): δ 157.4, 139.3, 126.4, 113.9, 102.8, 76.8, 73.4, 70.1, 68.6, 67.6, 67.4, 61.1, 29.3, 28.9, 28.8, 26.0, 25.5.

Alcohol M4. The crude electrolysis product was purified by chromatography on a silica gel column [eluent: ethanol–methanol (3 : 2 v/v)]. MS (ES): $C_{22}H_{33}O_9Na$ (calcd. 464.48). m/z 441.4 $[C_{22}H_{33}O_9]^-$. NMR ^{1}H (400 MHz, DMSO-d$_6$): δ 7.25 (d, 2H, J 8.4 Hz, arom), 6.88 (d, 2H, J 8.4 Hz, arom), 4.68 (m, 1H), 4.62 (s, 1H, H-sugar), 4.23 (d, 1H, J 5.4 Hz, H-sugar), 3.96 (t, 2H, J 6.6 Hz, CH$_2$OAr), 3.87 (br s, 1H, H-sugar), 3.78 (m, 1H, H-sugar), 3.75 (br s, 1H, H-sugar), 3.59 (m, 1H, CH$_2$O-sugar), 3.26 (m, 1H, CH$_2$O-sugar), 1.55–1.65 (m, 2H, CH$_2$), 1.25–1.55 (m, 13 H, CH$_2$ + CH$_3$).

Alcohol M5. In a round bottom flask equipped with a magnetic stirring bar were introduced 60 mL of ethanol (absolute). Ketone **K5** (440 mg, 2 mmol, 1 equiv.) and NaBH$_4$ (83 mg, 2.2 mmol, 1.1 equiv.) were successively added. The reaction was controlled by thin layer chromatography [eluent:

cyclohexane–ethyl acetate (4 : 1 v/v); R_f (**K5**) = 0.50; R_f (**M5**) = 0.28]. After 12 h stirring at 20 °C, water (150 mL) and a 2 M aqueous solution of HCl (2 mL) were added, then the aqueous layer was extracted with diethyl ether. The organic layer was washed with water, dried over MgSO$_4$ then filtered and concentrated under reduced pressure. The crude product was purified by chromatography on a silica gel column [eluent: cyclohexane–ethyl acetate (4 : 1 v/v)]. Compound **M5** was obtained as a yellow oil in 90% yield (400 mg). HRMS (EI): calcd $[C_{14}H_{22}O_2]^+$ 222.1620, found 222.1622. NMR ^{1}H (400 MHz, DMSO-d$_6$): δ 7.26 (d, 2H, J 8.4 Hz, arom), 6.88 (d, 2H, J 8.4 Hz, arom), 5.05 (d, 1H, J 4.4 Hz, OH), 4.68 (m, 1H), 3.96 (t, 2H, J 6.4 Hz, CH$_2$OAr), 1.72 (quint, 2H, J 6.9 Hz, CH$_2$), 1.45 (m, 2H, CH$_2$), 1.26–1.39 (m, 4H, CH$_2$), 1.32 (d, 3H, J 6.4 Hz, CH$_3$), 0.92 (t, 3H, J 5.9 Hz, CH$_3$). NMR ^{13}C (100 MHz, DMSO-d$_6$): δ 158.5, 137.8, 126.6, 114.4, 69.9, 68.0, 31.6, 29.3, 25.7, 25.0, 22.6, 14.0.

Electrochemical and physical analyses

A Tacussel PRT 100-1X potentiostat coupled with a Tacussel IG5-N integrator was used for controlled-potential electrolyses, which were performed in a three-compartment glass cell joined by two sintered glasses. The cathodic cell contained the ketone dissolved in 200 mL of buffer solution at a temperature of 30 °C. The cathode was a mercury pool of 42 cm^2 and the anode a graphite electrode. An aqueous saturated calomel electrode (SCE) was used as reference electrode. All aqueous solutions used were Britton–Robinson (BR) buffer solutions (pH = 3.4 and 9.5) with an ionic strength adjusted to 0.5 M by adding KCl. In some cases, a mixture of buffer–ethanol [1 : 1 v/v, pH = 3.6 and 10.1] was used in order to increase the solubility of the ketones. Stirring and N$_2$ flow were continued throughout the experiment. Detailed electrolysis conditions are summarised in Table 1. The evolution of electrolyses was followed by voltammetric checks and TLC. When the current densities drastically decreased, the electrolyses were stopped and the cathodic solution neutralised. In the case of glycosidic compounds **K1–4**, the solvents were evaporated under reduced pressure at 50 °C. For comparison, the non-glycosidic **K5** was also studied. The reduction products were extracted in these conditions with diethyl ether. Due to the fact that the electrolysis potential is close to the electrolyte discharge, the electricity consumption measurement is difficult. In all cases, it appears to be higher than expected for a one- or two-electron transfer (see Table 1). Reduction products were identified by TLC and the ^{1}H NMR spectra. The relative percentages of the unreacted ketones and of the reduction products were determined by measuring the intensity of well-defined ^{1}H NMR signals (for example, see Fig. 1).

Table 1 Electrolyses in protic medium at 30 °C

Entry	Substrate	Medium[a]	pH	Ketone % (K)	Alcohol % (M)	Pinacal % (D)	dl/meso	D/M	E_{appl}/ V vs. SCE	Electricity consumption/ F mol^{-1}
1	HeAc (**K5**)	A	3.6	52	7	41	0.46	5.86	−1.28	1.63
2	GluAcO3 (**K1**)	B	3.4	80	20	—			−1.28 → −1.30	2.56
3	HeAc (**K5**)	C	10.1	8	39	53	1.17	1.36	−1.70	2.33
4	GluAcO3 (**K1**)	C	10.1	15	85	—			−1.70	3.28
5	GluAcO8 (**K2**)	C	10.1	44	56	—			−1.70	2.97
6	MaltAcO8 (**K3**)	C	10.1	34	66	—			−1.70	3.35
7	GluAcO3 (**K1**)	D	9.5	16	84	—			−1.60	3.76
8	Na$^+$LacAcO8$^-$(**K4**)	D	8.6	—	100	—			−1.70	7.4
9	HeAc (**K5**) + **DOM**	E	9.5	28	41	31	1.27	0.76	−1.60	3.76

[a] Electrolyses medium A: BR–ethanol (50 : 50 v/v), $c = 1.4 \times 10^{-3}$ M, B: BR, $c = 1.4 \times 10^{-3}$ M, C: BR–ethanol (50 : 50 v/v), m (starting material) = 20–50 mg, D: BR, m = 20–50 mg, E: BR, 1×10^{-3} M **DOM**, $c = 1 \times 10^{-3}$ M
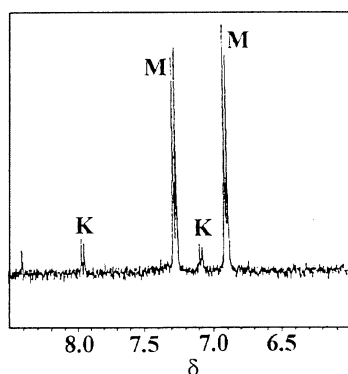

Fig. 1 Aromatic ^{1}H NMR signals of the crude products isolated after an exhaustive electrolysis of GluAcO3 (**K1**) at pH 10, E_{appl} = −1.70 V vs. SCE. (**K** residual ketone, **M** alcohol).

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 400 spectrometer. The high resolution mass spectrometry (HRMS, FAB+) was performed by the Service Central d'Analyse (CNRS Vernaison, France) and the ES mass spectroscopy by the Laboratoire de Spectrométrie de Masse Bio-Organique, Faculté de Chimie, at Strasbourg (France).

Computer modelling

The exploration of the conformational space of compound GluAcO3 in water and DMF solutions has been performed by using the Batchmin program within the MM2 force field of the Macromodel package.[8] The simulation in solution was carried out with the Silverware program of the Sybyl package.[9] The densities and the volumes of the aqueous and DMF solutions are 1.333 g cm^{-3}, 57 844 Å^3 and 0.778 g cm^{-3}, 55 819 Å^3, respectively. The temporal evolution of the distance O$_{46}$···H$_{41}$ has been studied in each case by a molecular dynamics simulation of 50 ps performed in the NVT ensemble (P = 1 atm, T = 300 K).

Results and discussion

Electrochemical reductions of aromatic ketones in aqueous medium give rise to the formation of two products: the monomeric alcohol (**M**) and the pinacol (**D**) with its two diastereomeric forms dl and $meso$. Depending on the electrolysis conditions, especially the pH of the solutions, the ratio **D/M** varies, leading mainly to the formation of the alcohol in neutral medium and of the pinacol in acidic or basic medium.[10]

The polarograms of the glycosides, previously published,[5] present at any pH a cathodic wave very close to the electrolyte discharge. The results of exhaustive electrolyses are summarised in Table 1 (acid medium, entries 1 and 2, basic medium, entries 3–9). As in our previous works,[5,6] **K5** is used as a reference compound. In all cases, variable amounts of

ketone remain at the end of the electrolysis. This amount increases with the alkyl chain length and is probably due to autoinhibition phenomena. Indeed, as observed on the polarographic curves (DC and AC), these ketones and their reduction products are strongly adsorbed at the electrode surface; this perturbation becomes more noticeable with compounds bearing a long alkyl chain (n = 8) and/or maltose as a polar head group.[5] In acidic medium, the amount of unreacted GluAcO3 turns out to be particularly important (>80%).

As expected, the electrolysis in an acidic medium of the model molecule **K5** at the reduction step involving a one-electron transfer, leads to the neutral radical, which dimerises to form the expected diastereomeric pinacols (**D5**) with little preference in the steric approach ($dl/meso$ = 0.5). Only traces of the corresponding alcohol are detected (Table 1, entry 1). In basic medium (entry 3) the electroreduction of this aromatic ketone leads to a mixture of the alcohol (**M5**) and pinacols (**D5**). The $dl/meso$ ratio, which is higher than that obtained in acidic medium, is similar to that reported for acetophenone in the same medium.[2] Indeed, $dl/meso$ ratios are known to depend on the pH conditions.[11,12]

However, electrolyses performed with glycosidic derivatives give unexpected results. When **K1** was reduced in acidic medium (entry 2), we observed exclusive formation of the alcohol (**M1**), suggesting that the duplication process of the neutral radical is completely hindered. On the other hand, electroreduction in basic medium of **K1–4** leads also to the sole formation of alcohols (**M1–4**) (Table 1, entries 4–8).

In order to test the possible role played by the glycosidic moieties, implying inter- or intramolecular interactions, we have performed the electroreduction of our model compound **K5** in the presence of the maltose surfactant 1-O-dodecyl-β-D-maltopyranoside (**DOM**) (Table 1, entry 9), which has a critical micellar concentration (CMC) of 0.15 mM.[13] For this system, only intermolecular interactions may exist. Under these conditions, the percentage of the alcohol (**M5**) increases but 31% of pinacol (**D5**) is still formed. The small decrease of the ratio (**D/M**) can be related to the solubilisation of the ketone inside the micellar structure. Indeed, the presence of **DOM**, at c > CMC, in the aqueous solution of **K5** causes changes in the shape and the current intensity of the AC and DC polarographic curves. In previous works, we studied the electroreduction, at pH = 10, of acetophenone and (4-acetylphenoxy) alkyltrimethyl ammonium salts in the presence of cetyltrimethyl ammonium salts.[1,2] Above the CMC it had been noted that, in comparison to the pure aqueous medium, the alcohol yield is slightly increased in the presence of the surfactants but the pinacol is always formed. The electroreducible moiety is probably included within mixed micelles which inhibit the influence of the basic medium or the change in solvation process. Moreover in this case, the improvement in yield of the two-electron product can be attributed to the stabilisation of the carbanion intermediate by the cationic

head group of the surfactant. With glucosidic compounds, this type of interaction does not exist. Other unusual interactions have to be considered to explain the very high chemioselectivity obtained with these compounds.

More generally, specific interactions between the acetyl group and the glycosidic polar head groups might be involved in the electrochemical process in basic as well as in acidic media. These interactions should be mainly intramolecular. It is well known that hydrogen bonds between water molecules and hydroxyl groups of saccharides can build intramolecular bridges.[14,15] Taking this into account, we can hypothesise a bent conformation for our electroreducible ketones favoured by interactions involving the carbonyl group, a hydroxyl function of the sugar moiety and water molecules. To support this hypothesis, we have realised a molecular dynamics calculation with the GluAcO3 molecule in water and, for comparison, in an aprotic solvent (DMF). In aqueous medium, the lowest energy conformations show the participation of the ketone, the primary hydroxyl group of the sugar unit and six water molecules [Fig. 2(a)]. Three water molecules build a solvation chain between the carbonyl function (O_{46}) and the primary alcohol of the sugar ($O_{24}H_{41}$), other water molecules are involved in the primary solvation shell. The temporal evolution of the distance $O_{46}\cdots H_{41}$, presented in Fig. 2(b), is maintained at 4 Å during the computational time of 50 ps. In an aprotic solvent (Fig. 3), the conformation of the molecule is more stretched out and a statistical value of about 9 Å is measured for the $O_{46}\cdots H_{41}$ distance.

The peculiar globular conformation of the electroreducible amphiphilic ketones in water may have a strong influence on the chemical reactions occuring after the electron transfer.
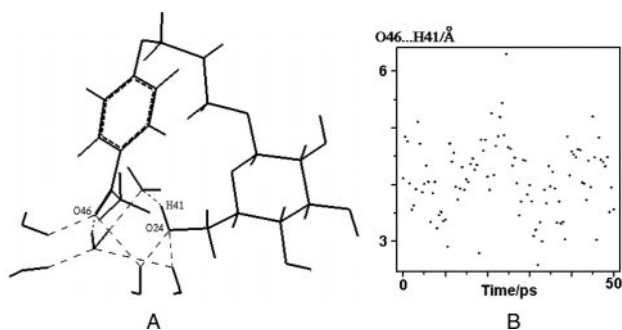

Fig. 3 (A) Conformation of GluAcO3 (K1) in DMF solution. (B) Temporal evolution of the $O_{46}\cdots H_{41}$ distance in DMF solution.

Fig. 2 (A) Conformation of GluAcO3 (K1) in aqueous solution. (B) Temporal evolution of the $O_{46}\cdots H_{41}$ distance in aqueous solution.

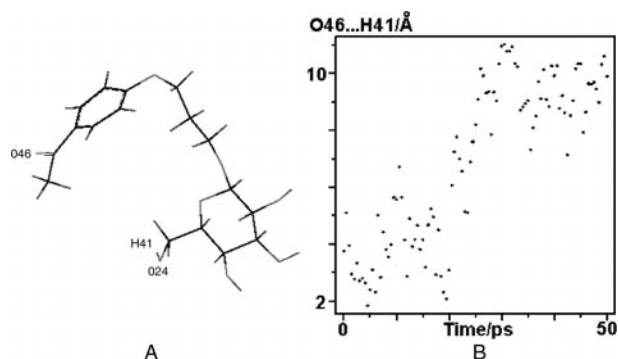In acidic medium, the neutral radical coupling appears to be definitively hindered in the case of GluAcO3, in contrast to HeAc under similar conditions. As shown in Table 1 (entry 2), the electricity consumption was much higher than the theoretical value corresponding to a one-electron transfer and a very large amount of ketone remains when the electrolysis was stopped. The strong steric hindrance due to the bridged conformation can prevent the dimerisation. The exclusive formation of alcohol could be explained by a slow disproportionation reaction of the neutral radical (Scheme 1), however it cannot explain the very poor faradaic yield and the high residual amount of ketone K1 (>80%). It seems more likely to suppose that, at the same applied potential, a second exchange of one electron may occur, probably in an absorbed phase. The fast protonation of the anion gives rise to the formation of the corresponding alcohol, which remains strongly adsorbed onto the electrode at this potential value and inhibits the reduction process.

In basic medium, the reduction is performed at a more negative potential value ($E_{appl} = -1.70$ V vs. SCE) and a competition exists between the dimerisation of the anion radical and its protonation. On account of the steric factor, the kinetic factor of the radical–radical coupling is very slow and the formation of the neutral radical becomes the exclusive process. At the fixed potential of -1.70 V, this latter is reduced to the corresponding carbanion with, as a consequence, the formation of the monomeric alcohol after protonation.
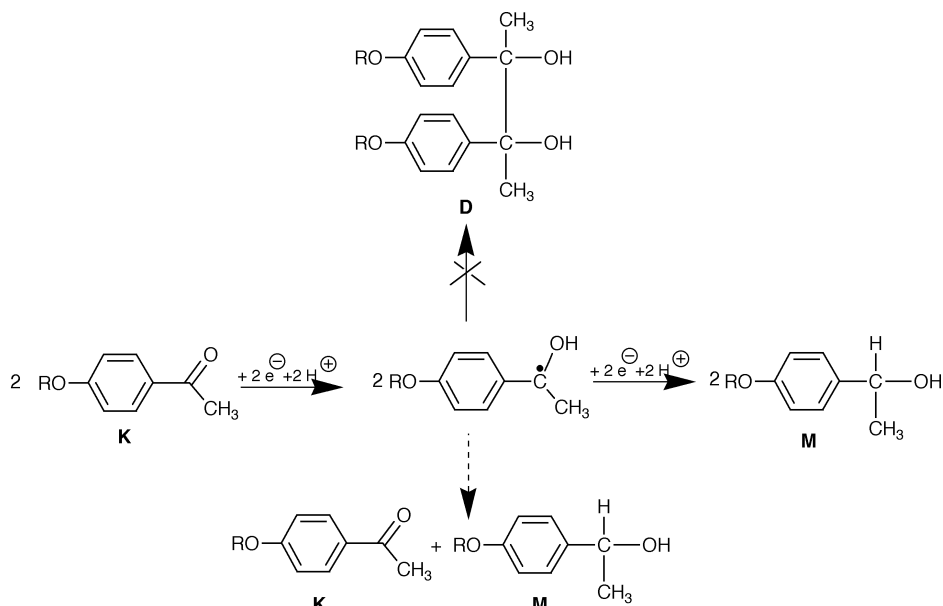
Scheme 2

Conclusion

In summary, the electrochemical reduction of amphiphilic sugar derivatives in aqueous medium has shown the important role played by the saccharidic moiety. The highly polar structure and the possibility to form intramolecular hydrogen bonds may stabilise a globular conformation. Molecular dynamics calculations of the solvent interactions support this hypothesis. In water, intramolecular interactions, between the hydroxyl group of sugar and the ketyl group by means of three water molecules, lead to a folded conformation of the molecule stabilised in a primary solvation shell consisting of three other water molecules. A consequence of this peculiarity is the exclusive formation of the monomeric alcohols after electrolysis of aromatic ketones in aqueous medium at any pH value. In contrast to aqueous solutions, the amphiphilic molecules show a very fast extension in aprotic solvents such as DMF. In this case, the sole reduction products are the diastereomeric pinacols.[6]

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