N,*N*′-Dimethyl-2,3-dialkylpyrazinium salts as redox-switchable surfactants? Redox, spectral, EPR and surfactant properties†

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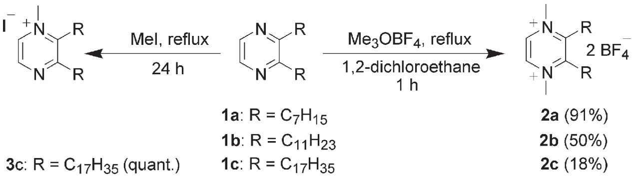
***N*,*N*′-Dimethyl-2,3-dialkylpyrazinium salts show reversible transitions between all redox stages and a monolayer formation at the air–water interface that suggests their use as redox-switchable surfactants.**

A firm comprehension of the reactivity patterns of radical ions[1] is invaluable for contriving extraordinarily stable redox systems as needed in various fields, *e.g.* in materials science,[2] molecular machines,[3] and for redox-switchable surfactants.[3] As for the latter field, ferrocenes[4] and viologens[5] have received most of the coverage due to the high stability of their various redox stages. Surprisingly, while pyrazinium salts[6] share a great deal of structural similarity with viologens, this redox system has attracted little attention, if we abstain from their benzannulated derivatives, the quinoxalinium systems.[7] Herein, we describe the redox properties, the long-term stability and the surfactant features of *N*,*N*′-dimethyl-2,3-dialkylpyrazinium tetrafluoroborates **2a–c** making them a new prototype of redox-switchable surfactants.

Methylation of pyrazines **1a–c**, obtained from the reaction of the corresponding diketones with ethylenediamine, with Meerwein's salt[6] yielded the corresponding 2,3-dialkylpyrazinium salts **2a–c**, while methylation with iodomethane afforded **3c** (Scheme 1).

Cyclic voltammetry studies at 100 mV s^{-1} unveiled two reversible reduction waves for **2a–c** at *ca.* −0.20 V (*vs.* Fc/Fc$^+$) and −1.16 V (*vs.* Fc/Fc$^+$) in acetonitrile that were assigned to the formation of the radical cation ($X^{+\bullet}$) and the diazine (X^0, Scheme 2), respectively. Assessment of the Nicholson–Shain criteria[8] (i_{red} *vs.* $v^{1/2}$ and current function *vs.* v; v = scan rate) for both reduction steps clearly supported an E_{rev} mechanism. The large separation of the two reduction waves pointed to a very good thermodynamic stabilisation of the radical cation intermediate towards disproportionation ($K_{disp} > 10^{-16}$).

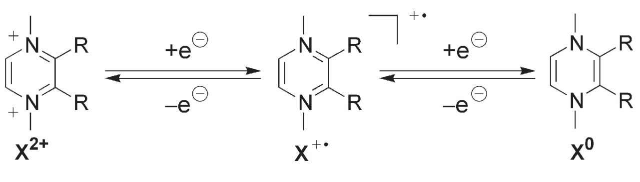


Scheme 1 Synthesis of mono- and dimethylated 2,3-dialkylpyrazinium derivatives.

Spectroelectrochemical reduction[9] of **2a** (X^{2+}) further confirmed the stability of all redox stages on a much more extended timescale (Fig. 1). Upon reduction, the spectra showed three isosbestic points indicative of a clean conversion of **2a** (X^{2+}) to **2a** ($X^{+\bullet}$). At even more negative potential **2a** (X^0) emerged with no absorption above 250 nm.

To investigate the long-term stability of $X^{+\bullet}$, **2a–c** ($X^{+\bullet}$) was prepared by mixing **2a–c** (X^{2+}) with powdered KI or KBr. The salts, dissolved in dichloromethane, showed strong bands at 265 nm and 333 nm (in line with $X^{+\bullet}$ generated in the spectroelectrochemical study) and a faint contourless absorption envelope between 500 and 750 nm that is responsible for their green colour.[10] The EPR spectrum of a fresh solution of **2c** ($X^{+\bullet}$) in $CHCl_3$ showed a multiplet with a *g*-value of 2.0032 typical for organic compounds (upper plot in Fig. 2B). DFT calculations using ADF 2002 (SCM, Inc.) suggested that the multiplet arises from a hyperfine coupling of the electron spin to the six hydrogens of the two *N*-methyl groups (computed: 0.85 mT, experimental: 0.8 mT, line fit in Fig. 2B). Within two hours, however, the EPR spectrum considerably broadened with the multiplet still appearing (Fig. 2B, lower plot). This line broadening may arise from intermolecular exchange[11] due to slow temperature-dependent aggregation of **2c** ($X^{+\bullet}$) cations. This was further corroborated by EPR measurements on a sample of **2b** ($X^{+\bullet}$) after keeping it for 1 year as a $CHCl_3$ solution at −40 °C (Fig. 2A). It showed a broad spectrum with a line width of 2.2 mT. The spectrum furnished strong evidence for the exceptional stability of the radical cations **2a–c** ($X^{+\bullet}$).

The redox stages of **2c** (X^{2+}, $X^{+\bullet}$ and X^0) can be expected to act as surfactants due to their lipid-like molecular structure. Equally, **1c** and **3c** with their long alkyl chains may arrange at the air–water interface to give compressible monolayers.[12] However, since **2c** is sensitive to water,[7] one has to stabilize it in 0.5–1 M sulfuric acid. The prospect of altering the charge of the pyrazinium headgroup



Scheme 2 Two sequential one-electron reductions of **2a–c** yielding the radical cation and the neutral X^0.

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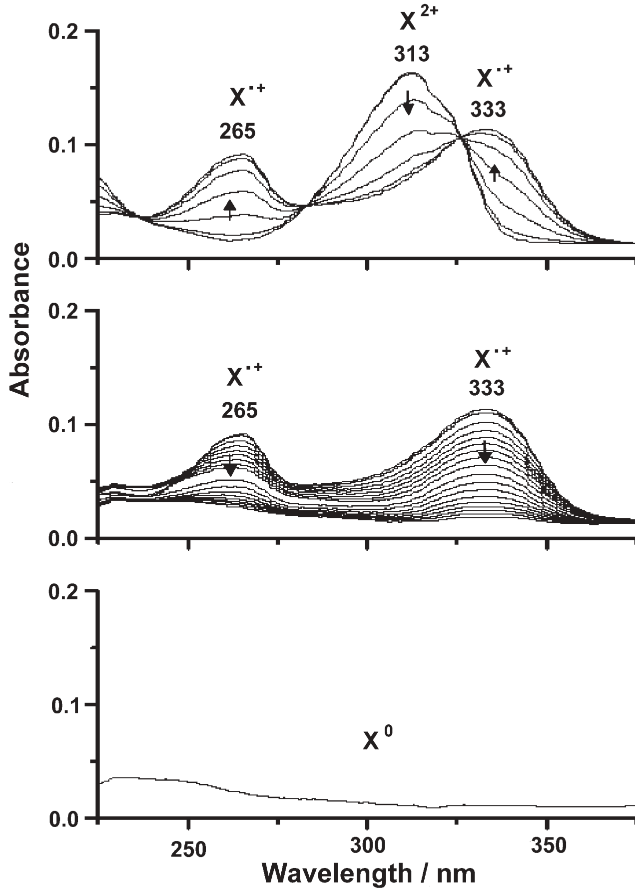

Fig. 1 Spectroelectrochemical changes upon reduction of **2a** (X^{2+}) in acetonitrile (0.1 M $n\text{Bu}_4\text{NPF}_6$). Top: disappearance of **2a** (X^{2+}) and formation of **2a** ($X^{+\bullet}$) at $E = -0.20$ V (*vs.* Fc/Fc$^+$). Middle: disappearance of **2a** ($X^{+\bullet}$) at $E = -1.16$ V (*vs.* Fc/Fc$^+$). Bottom: spectrum of **2a** (X^0).

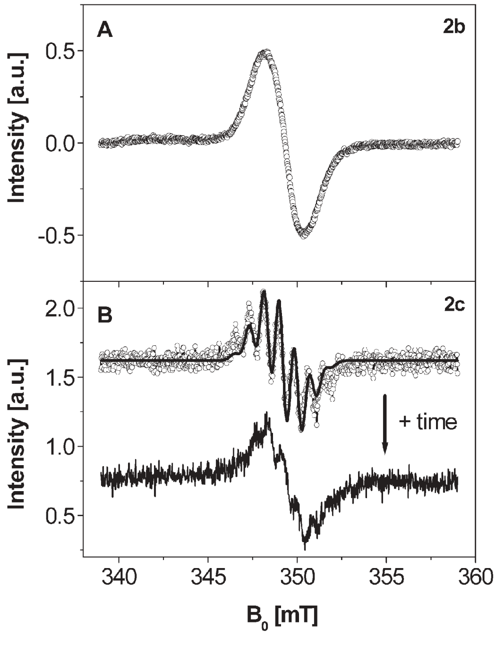

Fig. 2 EPR spectra of **2b** ($X^{+\bullet}$) dissolved in CHCl_3 after storage for 1 year at −40 °C (A) and of **2c** ($X^{+\bullet}$) recorded with a fresh solution (B, upper plot) and after 2 hours at RT (B, lower plot).

by redox cycles without changing the principal molecular structure characterizes this compound as a potential model to systematically study the role of electrostatic interactions on the phase behaviour of mono- or bilayers with the well-known Langmuir–Blodgett (LB) technique.[13] Due to the sensitivity of $X^{+\bullet}$ and X^0 to oxygen (inevitable in our LB experiment), we recorded isotherms of **1c** (as a model for X^0), **2c** and **3c** (as a model for $X^{+\bullet}$) (Fig. 3).

The monocharged pyrazinium surfactant **3c** exhibited a steep isotherm on pure water with a low compressibility. Roughly 36 Å^2 per molecule was the smallest area, which could be applied before film collapse. Consecutive compression–expansion cycles showed complete reversibility in the isotherms. The isotherm of its neutral counterpart **1c** exhibited an irreversible collapse at the highest pressure applied (50 mN m^{-1}). Also, a change in the slope showed up between 15 and 18 mN m^{-1}. In contrast, the bicharged compound **2c** could be compressed on pure water to areas as low as 13 Å^2 per molecule, passing two shoulders separated by a kink at 15 mN m^{-1}(left of arrow). A consecutive compression cycle showed a complete lack of the first broad shoulder but nearly the same smallest area (not shown). When 1 : 1 salts, such as NaCl, or 1 M H_2SO_4 were added to the water subphase in approximately 1 M concentration the second shoulder developed into a plateau, entered *via* a sharp kink (right of arrow).

This series of experiments showed that the monocharged pyrazinium salt has an amphiphilic character, which is highly suitable to form an insoluble monolayer as known from lipids. The non-charged pyrazinium salt also tended to form an insoluble monolayer but due to the missing charge in the headgroup it showed less tendency to stay coupled to the air–water interface: the monolayer collapsed at high pressures. The bicharged system finally was stabilized by 1 M H_2SO_4 as the subphase. Since the minimum area is too low for a double-chained surfactant, partial solubility or instability of the film can be assumed. This is supported by comparison with the stable isotherm of the monocharged compound, which shows up at reasonable molecular areas. The isotherm on an aqueous 1 M NaCl subphase looked the same as on H_2SO_4 but different from that on pure water. Therefore, we can conclude that the stabilizing effect is most probably due to a screening of electrostatic repulsion between the charged headgroups of the pyrazinium salt.[14] In summary, the redox system **2c** ($X^0 \rightleftharpoons X^{+\bullet}$) may become a useful novel redox-switchable surfactant system that can even be complemented by

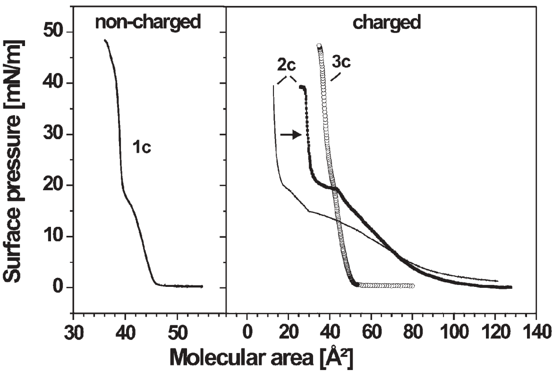

Fig. 3 Langmuir isotherms of **1c** and**3c** on pure water, and of **2c** on pure water (thin line) and on 1 M H_2SO_4 or 1 M NaCl (thick line) at 20 °C.

the third redox stage **2c** (X^{2+}), if special conditions are provided (*i.e.* reaction in 1 M sulfuric acid).

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