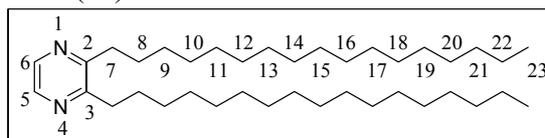


***N,N'*-Dimethyl-2,3-dialkylpyrazinium Salts as Redox-Switchable Surfactants? Redox, Spectral, EPR and Surfactant Properties**

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General synthesis of pyrazine derivatives 1a-c:

2,3-(Di-n-heptadecyl)pyrazine (1c):



Hexatriacontane-18,19-dione (1.0 g, 1.9 mmol) and ethylenediamine (0.2 ml, 2.1 mmol) were refluxed for 3 h in 15 ml of ethanol (in case of **1c**, 5 ml of benzene was added additionally to solubilise the diketone). The reaction was monitored by TLC; after consumption of the starting material the reaction mixture was cooled and MnO₂ (0.5 g, 6.0 mmol) and potassium hydroxide (0.1 g, 2.5 mmol) were added. The reaction mixture was refluxed for another 15 h. The reaction mixture was cooled, filtered through a pad of celite and concentrated. The crude product was purified by column chromatography with hexane : ethylacetate (60:40) as eluent. The pure product was obtained as a white solid in 72% yield (*R_f* = 0.83, M.P. = 43-44 °C). IR (KBr) ν / cm^{-1} = 2954, 2915, 2849, 1472, 1411, 1156, 1135, 1069, 872, 716. ¹H-NMR (CDCl₃, 200 MHz): δ / ppm = 0.87 (t, *J* = 6.6 Hz, 6H, H-23), 1.25 (s, 56H, H-9-22), 1.63-1.74 (m, 4H, H-8), 2.80 (t, *J* = 7.8 Hz, 4H, H-7), 8.30 (s, 2H, H-5, 6). ¹³C-NMR (CDCl₃, 50 MHz): δ / ppm , 14.1 (C-23), 22.7 (C-22), 29.7 (C-9-21), 31.9 (C-8), 34.5 (C-7), 141.2 (C-2, 3), 155.9 (C-5,6). HRMS: C₃₈H₇₂N₂, Calculated: 556.5696, Found: 556.5685.

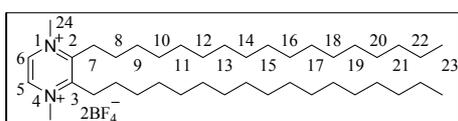
2,3-(Di-n-heptyl)pyrazine (1a):

1a was obtained as a yellow oil in 63% yield (*R_f* = 0.87). IR (KBr): ν / cm^{-1} = 3043 (CH, aromatic), 2956, 2927, 2855, 1465, 1407, 1378, 1232, 1148, 1073, 852, 714. ¹H-NMR (CDCl₃, 200 MHz): δ / ppm = 0.87 (t, ³*J* = 6.6 Hz, 6H, H-13), 1.28 (s, 16H, H-9-12), 1.63-1.74 (m, 4H, H-8), 2.80 (t, ³*J* = 7.6 Hz, 4H, H-7), 8.30 (s, 2H, H-5,6). ¹³C-NMR (CDCl₃, 50 MHz): δ / ppm = 14.1 (C-13), 22.6 (C-12), 28.9 (C-8), 29.1 (C-9), 29.6 (C-10), 31.7 (C-11), 34.5 (C-7), 141.2 (C-5, 6), 155.9 (C-2, 3). HRMS: C₁₈H₃₂N₂, Calculated: 276.2566, Found: 276.2559.

2,3-(Di-n-undecyl)pyrazine (1b):

1b was obtained as a colourless oil in 50% yield ($R_f = 0.89$). IR (KBr): $\nu / \text{cm}^{-1} = 3042$ (CH, aromatic), 2924, 2853, 1465, 1407, 1138, 851, 721. $^1\text{H-NMR}$ (CDCl_3 , 200 MHz): $\delta / \text{ppm} = 0.87$ (t, $J = 6.6$ Hz, 6H, H-17), 1.26 (s, 32H, H- 9-16), 1.62-1.74 (m, 4H, H-8), 2.81 (t, $J = 7.6$ Hz, 4H, H-7), 8.31 (s, 2H, H-5, 6). $^{13}\text{C-NMR}$ (CDCl_3 , 50 MHz): $\delta / \text{ppm} = 14.1$ (C-17), 22.7 (C-16), 29.0 (C-8), 29.6 (C- 9-14), 31.9 (C-15), 34.5 (C-7), 141.2 (C-5, 6), 155.9 (C-2, 3). HRMS: $\text{C}_{26}\text{H}_{48}\text{N}_2$ Calculated: 388.3818, Found: 388.3826.

General synthesis of the dimethylated pyrazinium salts 2a-c:



1,4-Dimethyl-2,3-(di-n-heptadecyl)pyrazinium tetrafluoroborate (2c): *2,3*-(Di-*n*-heptadecyl)-pyrazine (600 mg, 1.08 mmol) and trimethyloxonium tetrafluoroborate (400 mg, 2.69 mmol) in 25 ml of dry 1,2-dichloroethane were refluxed for 2 h. The solvent was evaporated and the residue was treated with dry ether yielding a white precipitate, which was filtered under nitrogen. The product was obtained as a white solid in 18% yield (M.P. = 192 °C). $^1\text{H-NMR}$ (CDCl_3 , 200 MHz): $\delta / \text{ppm} = 0.88$ (t, $J = 6.6$ Hz, 6H, H-23), 1.26 (s, 56H, H-9-22), 1.61-1.76 (m, 4H, H-8), 3.16 (m, 4H, H-7), 4.54 (bs, 6H, H-24), 9.29 (s, 2H, H-5, 6). $^{13}\text{C-NMR}$ (CDCl_3 , 50 MHz): $\delta / \text{ppm} = 14.1$ (C-23), 22.7 (C-22), 26.5 (C-21), 28.8 (C-9), 29.7 (C- 10-20), 31.9 (C-8), 36.0 (C-7), 70.6 (C-24), 161.3 (C-5,6). HRMS: $\text{C}_{40}\text{H}_{78}\text{N}_2^{+\bullet}$, Calculated: 586.6165, Found: 586.6156.

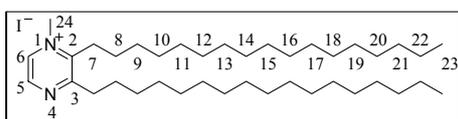
1,4-Dimethyl-2,3-(di-n-heptyl)pyrazinium tetrafluoroborate (2a): Obtained as a white solid in 91% yield (M.P. = 178 °C with decomposition). $^1\text{H-NMR}$ (CDCl_3 , 400 MHz): $\delta / \text{ppm} = 0.88$ (t, $^3J = 6.6$ Hz, 6H, H-13), 1.29 (s, 8H, H-11, 12), 1.36 (m, 4H, H-10), 1.54 (t, $^3J = 6.6$ Hz, 4H, H-9), 1.77 (bs, 4H, H-8), 3.18 (bs, 4H, H-7), 4.54 (bs, 6H, H-14), 9.27 (s, 2H, H-5,6). $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz): $\delta / \text{ppm} = 14.0$ (C-13), 22.5 (C-11, 12), 28.4 (C-9, 10), 29.8 (C-7, 8), 31.5 (C-14), 143.0 (C-5,6), 161.3 (C-2, 3). EA: $\text{C}_{20}\text{H}_{39}\text{B}_2\text{F}_8\text{N}_2^{+\bullet}$, Calculated: C 49.93; H 8.17; N 5.82; Found: C 49.35; H 7.68; N 5.79; HRMS: $\text{C}_{20}\text{H}_{38}\text{N}_2^{+\bullet}$: Calculated: 306.3035, Found: 306.3041.

1,4-Dimethyl-2,3-(di-n-undecyl)pyrazinium tetrafluoroborate (2b): White solid received in 50% yield, $^1\text{H-NMR}$ (CDCl_3 , 200 MHz): $\delta / \text{ppm} = 0.88$ (t, $J = 7.6$ Hz, 6-H, 17H), 1.26 (s, 32-H, 8-15H), 1.62-1.74 (m, 4-H, 16H), 2.81 (t, $J = 7.6$ Hz, 4-H, 7H), 8.31 (s, 2-H, 5,6H). ^{13}C -

NMR (CDCl₃, 50 MHz): δ / ppm = 15.1 (C-17), 23.7, 29.9, 30.3, 30.6, 32.9, 35.5 (C-7), 142.2 (C-5,6), 156.8 (C-2, 3). HRMS: C₂₈H₅₄N₂⁺: Calcd.: 418.430, Found: 418.425.

Synthesis of the monomethylated pyrazinium derivative 3c:

1-Methyl-2,3-(di-n-heptadecyl)pyrazinium iodide (3c):



2,3-(Di-*n*-heptadecyl)pyrazine (**1c**, 150 mg, 0.270 mmol) was refluxed in 15 ml of methyl iodide for 12 h. The reaction mixture was concentrated to yield a yellow solid in quantitative yield. Melting Point: 95-96 °C

IR (KBr): ν / cm⁻¹ = 2921, 1691, 1609, 1449, 1371, 1265, 1216, 1156, 1059, 1006, 848, 568.

¹H-NMR (CDCl₃, 200 MHz): δ / ppm = 0.87 (t, ³J = 6.2 Hz, 6H, H-23), 1.25 (s, 52H, H- 10-22), 1.54-1.85 (m, 8H, H-8, 9), 3.03 (t, ³J = 7.6 Hz, 2H, H-7'), 3.19 (t, ³J = 8.4 Hz, 2H, H-7), 4.63 (s, 3H, H-24), 9.09 (d, ³J = 3.0 Hz, 1H, H-5), 9.47 (d, ³J = 3.0 Hz, 1H, H-6). ¹³C-NMR (CDCl₃, 50 MHz): δ / ppm = 14.1 (C-23), 22.7 (C-22), 29.7 (C- 9-21), 31.9 (C-8), 34.5 (C-7), 141.2 (C-2, 3), 155.9 (C-5,6). EA: Calcd: C 67.02; H 10.82; N 4.01, Found: C 67.40, H 10.88, N 3.87.

Stability of 2 against water

To evaluate the properties of the pyrazinium salts as surfactants, their phase behaviour at the air-water interface in a Langmuir film balance was measured. Therefore, their chemical stability had to be assured. It has been reported earlier¹ that the solutions of dimethylpyrazinium tetrafluoroborates can be stabilised in water containing acid. Thus, the stability of pyrazinium salt **2a** (0.4 mM) was investigated in aqueous solution containing varying concentrations of sulphuric acid (10 mM-10 M). The degradation was followed qualitatively by recording changes in colour observed over a period of time and comparing it with the sample in pure acetonitrile. Solutions with high concentration of acid (between 2 M-10 M) were stable even after 2 weeks time (no visible colour change was observed). Interestingly, the solutions were colourless in sulphuric acid solution in contrast to pure acetonitrile solution that changed to green after 1 h (and showed precipitation of material after 2 weeks). Solutions containing 0.5 -1 M sulphuric acid showed a slight green colouration after 4 h, while solutions containing lower concentrations (0.1 M-10 mM) showed an immediate

green colouration (greener than the pure acetonitrile solution), which darkened with time. A precipitation was observed in the solutions with lower concentrations of the acid.

The stability of a solution of **2a** (0.5 M sulphuric acid) was monitored over a period of 11 h. The UV-Vis spectrum of the pyrazinium salt **2a** in sulphuric acid had a $\lambda_{\text{max}} = 319$ nm, which is similar to the one measured in dichloromethane ($\lambda_{\text{max}} = 317\text{-}318$ nm). The UV-Vis spectral changes were not very dramatic thus indicating that the pyrazinium salt **2a** was quite stable to the above conditions in water.

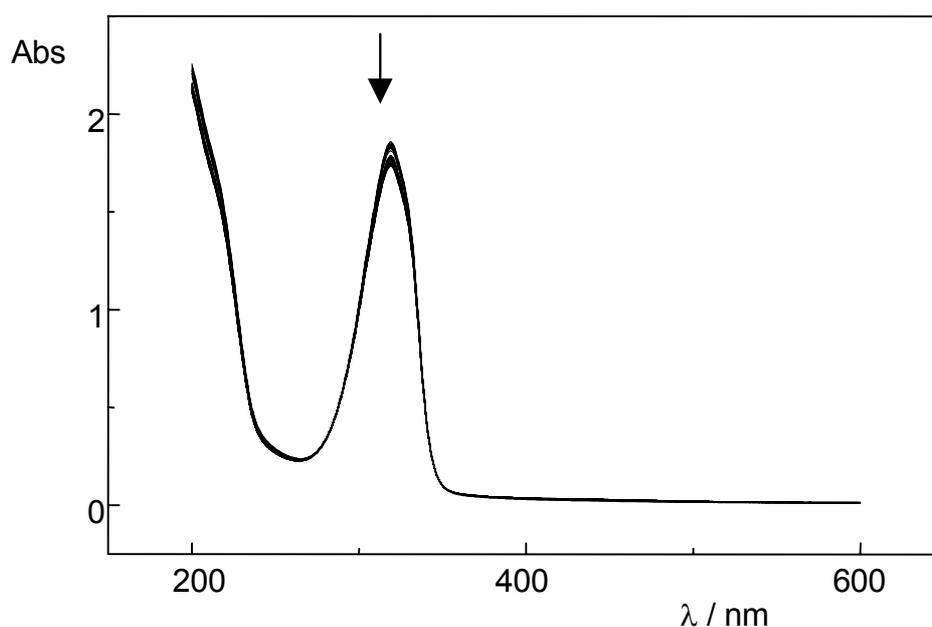
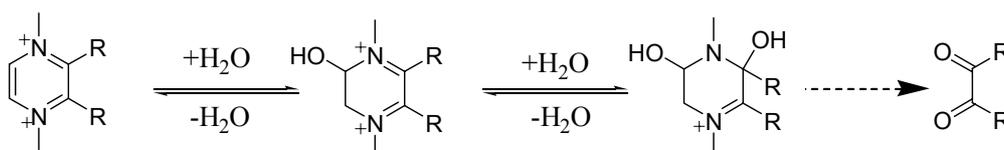


Figure 1. UV-Vis spectrum of **2a** in 0.5 M sulphuric acid. The spectrum is an overlay of 40 spectra measured over a period of 10 h with every measurement spaced by 15 min.

When a solution of **2a** in acetonitrile was diluted with water an immediate colour change resulted (colour changes from golden yellow to violet and finally to reddish brown). After 4-5 h a precipitate was observed (~30%) which when analysed ($^1\text{H-NMR}$) after isolation turned out to be the corresponding diketone.



Scheme 1: Proposed mechanism for the degradation of *N,N'*-dimethyl-2,3-dialkylpyrazinium tetrafluoroborates in presence of water.

Cyclic voltammetry investigations:

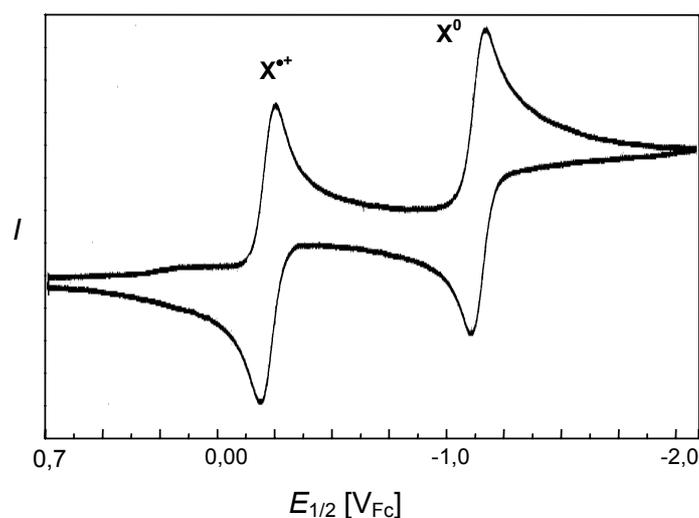


Figure 2. Cyclic voltammogram of **2a** in acetonitrile showing two completely reversible reduction waves.

Table 1: $E_{1/2}$ of N,N' -dimethyl-2,3-dialkylpyrazinium tetrafluoroborates in acetonitrile (*dichloromethane*) at 100 mV/s scan rate.

Pyrazinium derivative	$E_{1/2}$ [V vs. Fc/Fc ⁺]	$E_{1/2}$ [V vs. Fc/Fc ⁺]
2a	-0.20 (-0.16)	-1.16 (-1.21)
2b	-0.19	-1.14
2c	-0.19 (-0.15)	-1.16 (-1.25)

Nicholson-Shain diagnostic criteria² for N,N' -dimethyl-2,3-dialkylpyrazinium tetrafluoroborates:

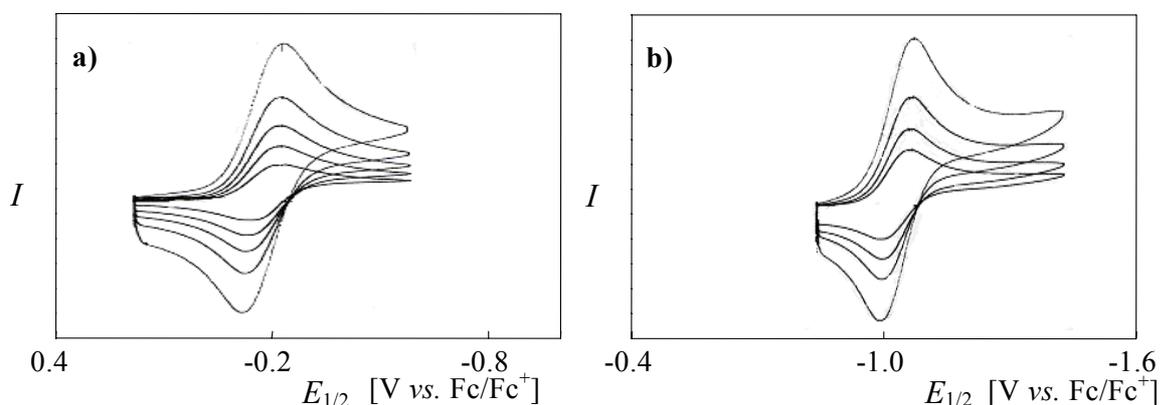


Figure 3. Scan rate dependence of the reduction waves in N,N' -dimethyl-2,3-dialkylpyrazinium tetrafluoroborates, a) the first reduction wave ($X^{\bullet+}$) and b) second reduction wave (X^0) of **2a** in acetonitrile (at 20, 50, 100, 200, 500 mV s⁻¹).

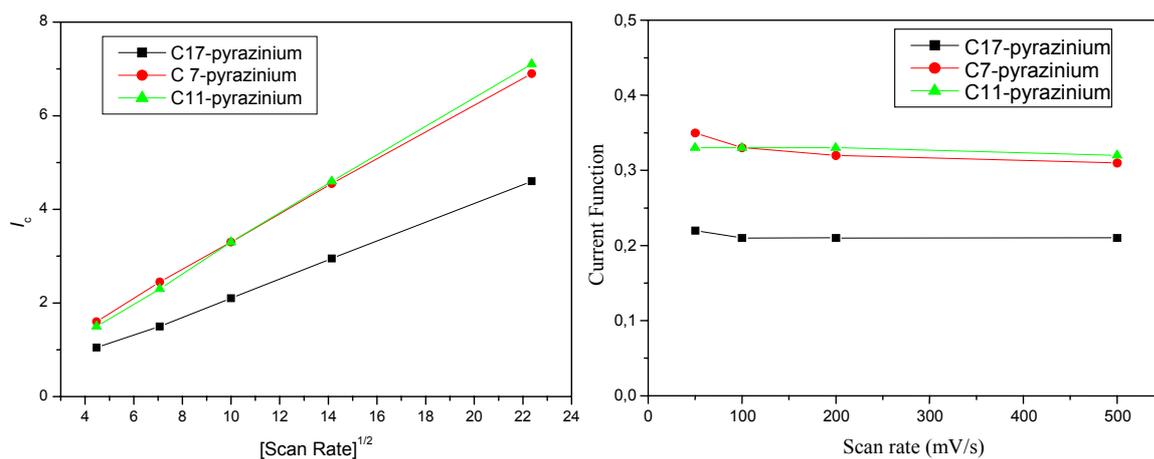


Figure 4. Scan rate dependence of the cathodic current in acetonitrile for the first reduction wave of **2a**, a) Plot of cathodic current (i_c) with $[\text{scan rate}]^{1/2}$, b) Plot of current function ($i_c/[\text{scan rate}]^{1/2}$) vs scan rate.

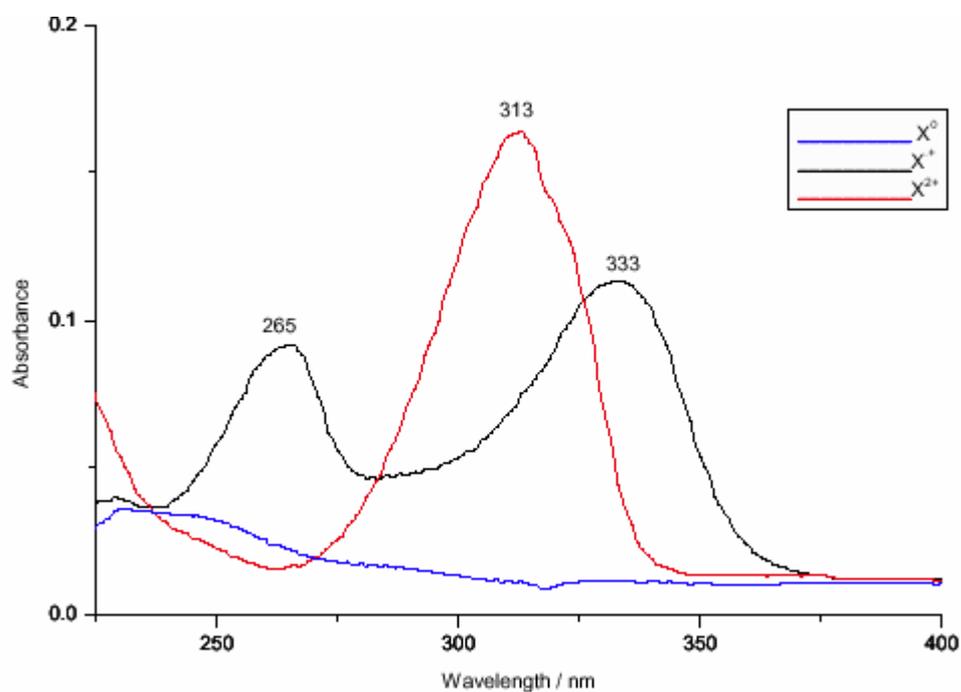


Figure 5. The absorption spectra of the redox stages X^{2+} , $X^{+\bullet}$ and X^0 (of **2a**) as obtained from the spectroelectrochemical investigation.

¹ T. J. Curphey, K. S. Prasad, "Di-quaternary Salts. I. Preparation and Characterisation of Di-quaternary Salts of some Diazines and Diazoles", *J. Org. Chem.* **1972**, *37*, 2259-2266.

² R. S. Nicholson and I. Shain, "Theory of Stationary Electrode Polarography", *Anal. Chem.* **1964**, *36*, 706-723.