On the effect of ion pairing of Keggin type polyanions with quaternary ammonium cations on redox potentials in organic solvents

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Electronic Supplemental Information

Syntheses

{(C₈H₁₇)₄N}⁺NCIO₄
A 50 mL ethanol solution containing (C₈H₁₇)₄NBr (9.76 g, 17.8 mmol) and 5 mL of a 6 M(aqueous) NaClO₄ water solution (6 M) were mixed with stirring. Water was added to precipitate (C₈H₁₇)₄NCIO₄ that was collected as a white solid by filtration. This ion exchange process was repeated twice. The combined white solids were crystallized from hot mixture of water and ethanol, offering colorless plate-like crystals, which were dried under vacuum at 90 °C for 5h. Yield was 8.90g, 88.5%. Anal. Calcd. for C₅₂H₆₈NClO₄: C, 67.86; H, 12.10; N, 2.47; Found: C, 68.48; H, 11.44; N, 2.01. ¹H NMR (400 MHz, CDCl₃): 3.27 – 3.12 (m, 8H), 1.63 (br, 8H), 1.43 – 1.19 (m, 40H), 0.88 (t, J = 6.8 Hz, 12H). ¹³C NMR (400 MHz, CDCl₃): 62.04, 59.07, 31.76, 29.15, 29.12, 26.40, 22.72, 22.12, 14.19.

{(C₈H₁₇)₃CH₃}⁺NCIO₄
(C₈H₁₇)₃CH₃NCl (21.32 g, 52.7 mmol) was dissolved in 100 mL toluene and 10 mL of a 4.6 M(aqueous) NaClO₄ solution was added. The mixture was stirred vigorously for 10 min and the water layer was removed. This treatment was repeated twice. The combined organic layers were washed with water three times. Toluene was removed by rotary evaporation, offering a yellow solid. The solid was crystallized from toluene, and dried under vacuum at 80 °C for 5h, the product was obtained as light yellow (14.02 g, 56.9%). Anal. Calcd. for C₅₂H₆₄NClO₄: C, 64.14; H, 11.63; N, 2.99; Found: C, 64.69; H, 11.90; N, 2.52. ¹H NMR (400 MHz, CDCl₃): 3.32 – 3.20 (m, 6H), 3.11 (s, 3H), 1.75 – 1.62 (m, 6H), 1.45-1.18 (m, 30H), 0.87 (t, J = 6.5 Hz, 9H). ¹³C NMR (400 MHz, CDCl₃): 62.04, 48.86, 31.87, 29.28, 29.24, 26.48, 22.81, 22.56, 14.28.

{(C₈H₁₇)₄}⁺NPF₆
A 4 mL dichloromethane solution of (C₈H₁₇)₄NBr (0.20g, 0.37 mmol) was mixed with 2 mL of a 1 M (aqueous) NH₄PF₆ solution. The mixture was stirred vigorously for 10 min, the water layer was removed, and this treatment was repeated twice. The organic layer was washed with water three times, dichloromethane was removed by evaporation and the light yellow solid was dried under vacuum at 80 °C for 3h (0.16 g, 71.4%). Anal. Calcd. for C₅₂H₆₈NPF₆: C, 62.82; H, 11.20; N, 2.29; Found: C, 62.99; H, 11.35; N, 1.70. ¹H NMR (400 MHz, CDCl₃): 3.18 - 3.08 (m, 8H), 1.60 (m, 8H), 1.42-1.38 (m, 40H), 0.88 (t, J = 6.8 Hz, 24H). ¹³C NMR (101 MHz, CDCl₃): 59.05, 31.84, 29.20, 26.42, 22.81, 22.10, 14.28. ¹⁹F NMR (377 MHz, CDCl₃) δ 89.27 (d, J₁₋₂ = 712.8 Hz). ³¹P NMR (162 MHz, CDCl₃) -143.87 (m, J₀₋₁ = 712.8 Hz).

{(C₈H₁₇)₃}⁺CH₃PF₆
The compound was prepared from (C₈H₁₇)₃CH₃NCl by the same method as (C₈H₁₇)₄NPF₆.
Anal. Calcd. for C₂₅H₃₄PF₆: C, 58.46; H, 10.60; N, 2.73; Found: C, 59.01; H, 10.80; N, 2.25. ¹H
TGA, cation content exptl. 45.0%, calcd for ((C8H17)4N)3Br 45.7%. IR (cm⁻¹): 3058, 2927, 2872, 2853, 1482, 1468, 1378, 994, 953, 903, 824.

[(C8H17)4N]3PW12O40
A 3 mL water solution of H3PW12O40·nH2O (0.20 g) and a 2 mL dichloromethane solution of (C8H17)4NBr (68 mg, 0.12 mmol, ca. 0.6 eqv.) were mixed and stirred vigorously for 5 min. The organic layer was washed with water several times until the water layer become neutral using a pH indicator. Dichloromethane was removed by evaporation. The colorless solid was dried under vacuum at 80 °C for 3h.

TGA, cation content exptl. 33.6%, calcd for ((C8H17)4N)2O 33.3%. IR (cm⁻¹): 2955, 2927, 2872, 2853, 1484, 1467, 1377, 1080, 985, 977, 896, 817.

[(C8H17)3CH3N]3PW12O40
The compound was prepared from H3PW12O40·nH2O and (C8H17)3CH3NCl by the same method as [(C8H17)4N]3PW12O40.

TGA, cation content exptl. 28.3%, calcd for ((C8H17)3CH3N)2O 28.3%. IR (cm⁻¹): 3040, 2953, 2926, 2869, 2856, 1482, 1466, 1377, 1079, 989, 980, 895, 816.

[(C8H17)4N]3SiW12O40
The compound was prepared from H4SiW12O40·nH2O by the same method as [(C8H17)4N]3PW12O40.

TGA, cation content exptl. 39.9%, calcd for ((C8H17)4N)2O 40.0%. IR (cm⁻¹): 2954, 2925, 2869, 2855, 1482, 1466, 1377, 1011, 970, 919, 883, 798.

[(C8H17)3CH3N]3SiW12O40
The compound was prepared from H4SiW12O40·nH2O by the same method as [(C8H17)3CH3N]3PW12O40.

TGA, cation content exptl. 34.6%, calcd for ((C8H17)3CH3N)2O 34.4%. IR (cm⁻¹): 3038, 2954, 2926, 2868, 2855, 1467, 1377, 1009, 968, 919, 882, 800.

K5BW12O40·11H2O was prepared according to Copaux’s method as modified in the literature (C. Rocchiccioli-Deltcheff; M. Fournier; R. Franck; R. Thouvenot. Inorg. Chem. 1983, 22, 207.

[(C8H17)4N]3BW12O40
K5BW12O40·11H2O (0.30 g, 92 umol) was dissolved in 3 mL water (pH~8, adjusted by NaHCO3 before the polyoxometalate was added). Then a 2 mL dichloromethane solution of (C8H17)4NBr (0.15 g, 0.28 mmol, 0.6 eqv.) was added. The mixture was stirred vigorously for 5 min, and the organic layer was washed with water (pH~8, adjusted by NaHCO3) two times. Dichloromethane was removed by evaporation. The colorless solid was dried under vacuum at 80 °C for 3h.

TGA, cation content exptl 45.7%, calcd for ((C8H17)4N)2O 45.7%. IR (cm⁻¹): 2954, 2926, 2868, 2855, 1482, 1468, 1378, 994, 953, 903, 824.
\[ [(C_{8}H_{17})_3CH_3N]_3BW_{12}O_{40} \]
The compound was prepared in the same way as \([(C_{8}H_{17})_4N]_3BW_{12}O_{40} \) form K\(_5\)BW\(_{12}O_{40}\cdot11\)H\(_2\)O\. TGA, cation content exptl 39.8\%, calcd for \([(C_{8}H_{17})_3CH_3N]_2O \) 40.0\%. IR (cm\(^{-1}\)): 3039, 2955, 2925, 2868, 2855, 1483, 1467, 1378, 991, 949, 898, 822.

\[ K_4PVW_{11}O_{40}\cdot2H_2O \] was prepared from H\(_3PW_{12}O_{40}\), according to the published method (P. J. Domaille. J. Am. Chem. Soc. 1984, 106, 7677.)

\[ [(C_{8}H_{17})_4N]_4PVW_{11}O_{40} \]
The compound was prepared from K\(_4\)PVW\(_{11}O_{40}\cdot2H_2O \) by the same method as \([(C_{8}H_{17})_4N]_3PW_{12}O_{40} \).
TGA, cation content exptl 41.0\%, calcd for \([(C_{8}H_{17})_4N]_3O \) 41.2\%. IR (cm\(^{-1}\)): 2954, 2926, 2868, 2855, 1482, 1466, 1378, 1094, 1067, 962, 887, 808, 519.

\[ [(C_{8}H_{17})_3CH_3N]_4PVW_{11}O_{40} \]
The compound was prepared from K\(_4\)PVW\(_{11}O_{40}\cdot2H_2O \) by the same method as \([(C_{8}H_{17})_3CH_3N]_3PW_{12}O_{40} \).
TGA, cation content exptl 35.0\%, calcd for \([(C_{8}H_{17})_4N]_3O \) 35.7\%. IR (cm\(^{-1}\)): 3041, 2956, 2924, 2871, 2857, 1483, 1467, 1376, 1094, 1068, 955, 888, 808, 519.
Figure S1. Cyclic voltammetry scans of 2mM C83-PW12O40 in dichloromethane at scanning rates ranging from 5 mV/s to 200 mV/s. Electrolyte 0.1 M (C8H17)3CH3NClO4; Ar, 20 °C; Pt working electrode; Ag/AgCl in 3.0 M KCl water solution reference electrode; counter electrode - Pt wire.

Figure S2. The dependence of oxidation and reducing peak current of C83-PW12O40 on the square root of scan rate.
**Figure S3.** Cyclic voltammetry scans of C84-PW_{12}O_{40} in dichloromethane at scanning rates ranging from 5 mV/s to 200 mV/s. Electrolyte 0.1 M C_{8}H_{17}NCIO_{4}; Ar, 20 °C; Pt working electrode; Ag/AgCl in 3.0 M KCl water solution reference electrode; counter electrode - Pt wire.

**Figure 4s.** The dependence of oxidation and reducing peak current of C84-PW_{12}O_{40} on the square root of scan rate.
Table S1. The reduction/oxidation potentials of C83-PW$_{12}$O$_{40}$ and C84-PW$_{12}$O$_{40}$ in dichloromethane at scanning rate from 5 mV/s to 200 mV/s in dichloromethane solution.

<table>
<thead>
<tr>
<th>Scanning rate</th>
<th>$E_{\text{red}}$</th>
<th>$E_{\text{ox}}$</th>
<th>$E_{1/2}$</th>
<th>$E_{\text{red}}$</th>
<th>$E_{\text{ox}}$</th>
<th>$E_{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 mV/s</td>
<td>-0.248</td>
<td>-0.139</td>
<td>-0.194</td>
<td>-0.360</td>
<td>-0.281</td>
<td>-0.321</td>
</tr>
<tr>
<td>25 mV/s</td>
<td>-0.267</td>
<td>-0.117</td>
<td>-0.192</td>
<td>-0.367</td>
<td>-0.276</td>
<td>-0.322</td>
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<tr>
<td>50 mV/s</td>
<td>-0.281</td>
<td>-0.097</td>
<td>-0.189</td>
<td>-0.371</td>
<td>-0.271</td>
<td>-0.321</td>
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<tr>
<td>75 mV/s</td>
<td>-0.294</td>
<td>-0.086</td>
<td>-0.190</td>
<td>-0.376</td>
<td>-0.267</td>
<td>-0.322</td>
</tr>
<tr>
<td>100 mV/s</td>
<td>-0.302</td>
<td>-0.078</td>
<td>-0.190</td>
<td>-0.379</td>
<td>-0.264</td>
<td>-0.322</td>
</tr>
<tr>
<td>200 mV/s</td>
<td>-0.325</td>
<td>-0.046</td>
<td>-0.186</td>
<td>-0.390</td>
<td>-0.255</td>
<td>-0.323</td>
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Table S2. Dielectric constant$^1$ and Kamlet-Taft$^2$ parameter sets.

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<th>Solvent</th>
<th>Dielectric constant</th>
<th>Kamlet-Taft parameter</th>
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<tr>
<td></td>
<td>$\pi^*$</td>
<td>$\alpha$</td>
</tr>
<tr>
<td>Chloroform</td>
<td>4.8</td>
<td>0.58</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>8.9</td>
<td>0.82</td>
</tr>
<tr>
<td>Pyridine</td>
<td>12.9</td>
<td>0.87</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>18.2</td>
<td>0.76</td>
</tr>
<tr>
<td>Acetone</td>
<td>20.6</td>
<td>0.71</td>
</tr>
<tr>
<td>2-nitropropane</td>
<td>25.5</td>
<td>NF</td>
</tr>
<tr>
<td>DMF</td>
<td>36.7</td>
<td>0.88</td>
</tr>
<tr>
<td>DMSO</td>
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<td>1.00</td>
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Table S3. Viscosity of the deuterated solvents at 25°C.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>CD$_2$Cl$_2$ $^3$</th>
<th>Acetone-$d_6$ $^4$</th>
<th>DMSO-$d_6$ $^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity (cP)</td>
<td>0.417</td>
<td>0.326</td>
<td>1.99</td>
</tr>
</tbody>
</table>

1. Ian M. Smallwood, Handbook of organic solvent properties.
**Figure S5.** UV-Vis absorption spectra in various solvents. $2 \times 10^{-5}$ M C83-PW$_{12}$O$_{40}$ (solid line) and C84-PW$_{12}$O$_{40}$ (dashed line).

**Figure S6.** $^1$H and $^{31}$P DOSY NMR signal decays of C84-PW$_{12}$O$_{40}$ (orange) and C83-PW$_{12}$O$_{40}$ (green) in DMSO (a), acetone (b) and dichloromethane solutions (c). The solid triangles refer $^1$H signals, and the hollow triangles refer to $^{31}$P signals. The solid line is the linear fitting of the data according to Stejskal-Tanner equation.
Figure S7. $^1$H and $^{31}$P DOSY NMR signal decays of C84-PF$_6$ (orange) and C83-PF$_6$ (green) in DMSO (a), acetone (b), dichloromethane solutions (c). The solid triangles refer $^1$H signals, and the hollow triangles refer to $^{31}$P signals. The solid line is the linear fitting of the data according to Stejskal-Tanner equation.