

**Cation and Pressure Effects on the Electrochemistry of 12-Tungstocobaltate and
12-Tungstophosphate Ions in Acidic Aqueous Solution**

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Supporting Information

Table S1. Mean diffusion coefficients $D/10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for the aqueous $\text{CoW}_{12}\text{O}_{40}^{5-/6-}$ couple^a

Medium	Concentration of supporting electrolyte/mol L ⁻¹			
	0.10	0.20	0.50	1.00
HClO ₄	2.3 ± 0.1	2.5 ± 0.1	2.3 ± 0.1	2.6 ± 0.1
HClO ₄ ^b	2.8 ± 0.1	2.7 ± 0.1	2.7 ± 0.1	(2.6 ± 0.1)
NH ₄ ClO ₄ ^c	2.5 ± 0.1	2.3 ± 0.1	2.3 ± 0.1	2.4 ± 0.1
LiClO ₄ ^c	1.8 ± 0.1	2.0 ± 0.1	1.9 ± 0.1	1.9 ± 0.1
NaClO ₄ ^c	2.1 ± 0.1	2.2 ± 0.1	2.0 ± 0.1	2.7 ± 0.1
KCl ^c	2.2 ± 0.1	2.4 ± 0.1	2.3 ± 0.1	2.6 ± 0.2
RbCl ^c	2.5 ± 0.1	2.6 ± 0.1	2.6 ± 0.1	2.3 ± 0.1
CsCl ^c	2.6 ± 0.1	2.9 ± 0.1	— ^d	— ^d
Mg(ClO ₄) ₂ ^c	2.5 ± 0.1	2.4 ± 0.1	3.3 ± 0.1	2.3 ± 0.1
CaCl ₂ ^c	1.6 ± 0.4	1.5 ± 0.1	1.7 ± 0.1	— ^e
Eu(NO ₃) ₃ ^f	1.9 ± 0.1	2.0 ± 0.1	1.7 ± 0.1	— ^e

^a0.1 MPa, 25.0 °C; [K₆CoW₁₂] = 1.0 mmol L⁻¹. ^bIonic strength adjusted to 1.00 mol L⁻¹ with NaClO₄. ^c0.001 mol L⁻¹ HClO₄ present. ^dCs₆CoW₁₂ insufficiently soluble. ^eAnodic CV maxima encroached upon O₂ evolution potentials. ^f0.10 mol L⁻¹ HClO₄ present.

Table S2. Volumes of activation $\Delta V_{\text{diff}}^{\ddagger}/\text{cm}^3 \text{ mol}^{-1}$ for diffusion of the aqueous $\text{CoW}_{12}\text{O}_{40}^{5-/6-}$ couple^a

Medium	Concentration of supporting electrolyte/mol L ⁻¹			
	0.1	0.2	0.5	1.0
HClO ₄	-1.0 ± 0.9	-1.8 ± 0.4	-1.8 ± 0.5	-1.9 ± 0.6
HClO ₄ ^b	0.6 ± 0.2	0.5 ± 0.3	0.0 ± 0.4	(-1.9 ± 0.6)
NH ₄ ClO ₄ ^c	-0.5 ± 0.5	-2.0 ± 0.5	-2.4 ± 0.3	-1.1 ± 0.5
LiClO ₄ ^c	-1.9 ± 1.0	-0.9 ± 0.8	-1.2 ± 0.4	-1.9 ± 0.4
NaClO ₄ ^c	-0.3 ± 0.2	-1.0 ± 0.7	0.9 ± 0.6	1.2 ± 0.2
KCl ^c	0.7 ± 0.6	-0.5 ± 0.4	-1.2 ± 0.1	— ^d
RbCl ^c	-0.8 ± 0.5	-1.2 ± 0.8	-0.4 ± 0.7	-2.7 ± 0.7
CsCl ^c	-1.3 ± 0.2	-2.9 ± 0.6	— ^e	— ^e
Mg(ClO ₄) ₂ ^c	-0.5 ± 0.3	1.1 ± 0.7	-1.3 ± 0.3	-0.9 ± 0.3
CaCl ₂ ^c	0.4 ± 0.5	-0.6 ± 0.7	-2.8 ± 0.8	— ^d
Eu(NO ₃) ₃ ^f	-0.6 ± 0.4	0.5 ± 1.4	-2.0 ± 0.3	— ^d

^a0-204 MPa, 25.0 °C, [K₆CoW₁₂] = 1.0 mmol L⁻¹; $\Delta V_{\text{diff}}^{\ddagger}$ from slopes of ln D vs. P plots.

^bIonic strength adjusted to 1.00 mol L⁻¹ with NaClO₄. ^c0.001 mol L⁻¹ HClO₄ present.

^dAnodic CV maxima encroached upon O₂ evolution potentials. ^eCs₆CoW₁₂ insufficiently soluble. ^f0.10 mol L⁻¹ HClO₄ present.