Electronic Supplementary Material (ESI) for Analytical Methods

Supporting Information

A Polymeric Membrane Electrode for the Detection of Perchlorate in Water at the Sub-micro-molar Level

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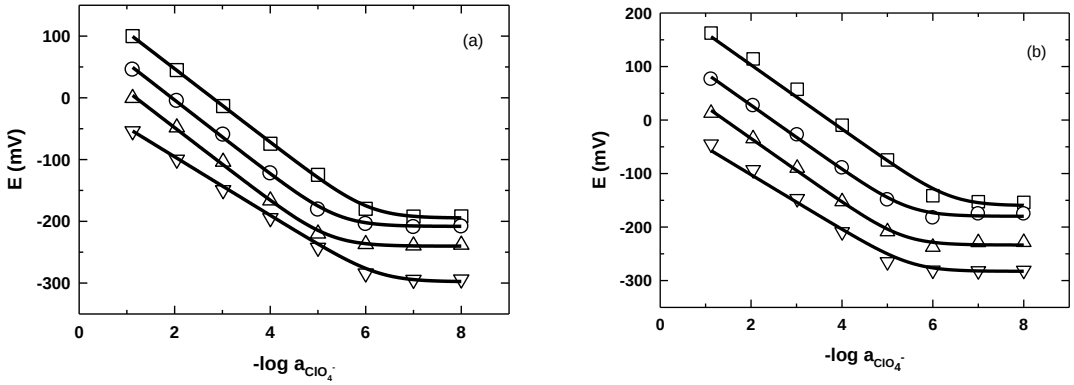
S1. Internal solution

Two types of internal solutions were tested, (1) perchlorate solution and (2) $Ni(DBM)_2$ + perchlorate, to optimize the sensitivity of perchlorate-ISE. Results (Fig S1 and Table S1 showed that 10^{-4} M of internal solution without addition of Ni(II) complexes was adequate in attaining Nernstian slope response and sensitivity.



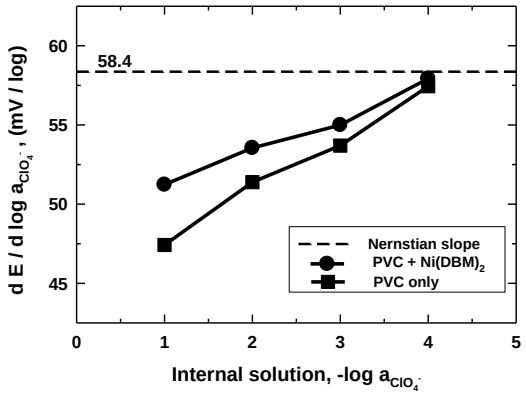


Fig. S1: Effect of internal perchlorate concentration on the potentiometric response of (a) PVC, (b) PVC+Ni(DBM)$_2$ electrode and (c) changes of Nernstian slope. Experimental conditions: temperature = 21 ~ 23 ^{o}C; pH = 5 ~7. Symbols: (□) 0.1 mM, (○) 1.0 mM, (△) 10 mM, (▽) 100 mM. The dashed line represents the theoretical Nernstian slope of 58.4 mV/log.

S2. Thickness of ISE membrane

The electrode potential decreased with perchlorate activity (log) in the perchlorate activity range of 10^{-6} to 10^{-1} M (Fig. S3, Supporting Information). The membrane resistance will increase with thickness which consequently will decrease the ion flux across the membrane.

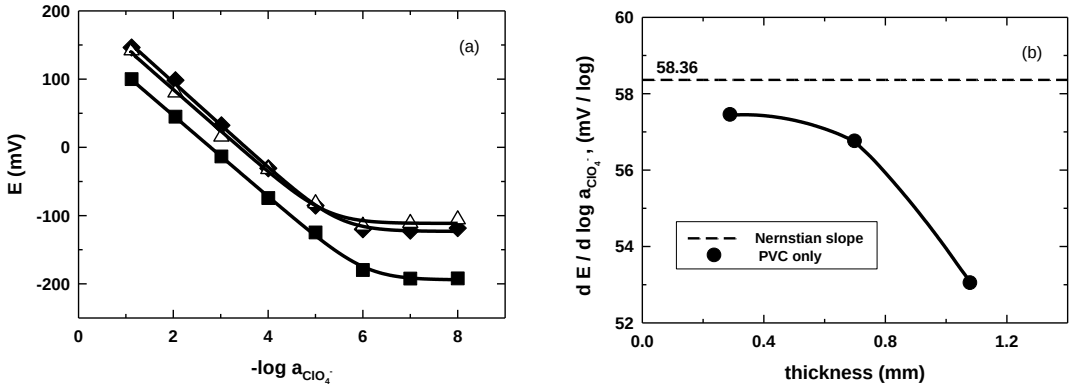


Fig. S2: Effect membrane thickness on the (a) potentiometric response and (b) Nernstian slope of PVC-only electrodes. Experimental conditions: temperature = 21~23 ^{o}C; pH = 6 ~7. Thickness: (■) 0.29 mm; (◆) 0.70 mm and (△) 1.08 (mm).

S3. Perchlorate adsorption by various membranes

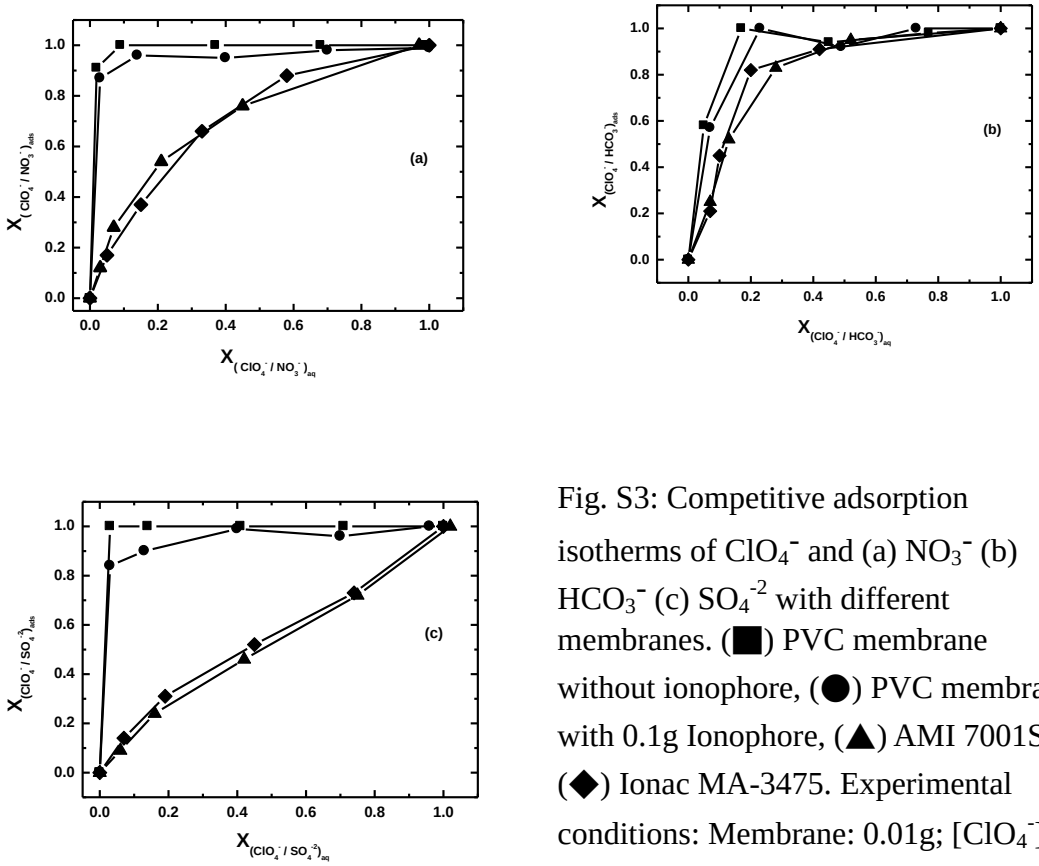


Fig. S3: Competitive adsorption isotherms of ClO_4^- and (a) NO_3^- (b) HCO_3^- (c) SO_4^{-2} with different membranes. (■) PVC membrane without ionophore, (●) PVC membrane with 0.1g Ionophore, (▲) AMI 7001S, (◆) Ionac MA-3475. Experimental conditions: Membrane: 0.01g; [ClO_4^-]: 0 to 10 ppm; [NO_3^-], [HCO_3^-] and [SO_4^{-2}]: 0 to 10 ppm; pH = 5 ~7.

Table S1. Effect of ionophore and presence of perchlorate in the internal solution on the performance of the PVC-only and the PVC+ionphore electrodes.

Membrane	Internal solution	Nernstian Slope (mV/log)	Linear range (M)	R^2
PVC [a]	DIW	60.6 ± 0.1	1.0×10^{-6} to 1.0×10^{-1}	0.9971
PVC [a]	ClO_4^- (10^{-4} M)	58.5 ± 0.3	1.0×10^{-6} to 1.0×10^{-1}	0.9964
PVC [a]	ClO_4^- (10^{-4} M) + ionophore (10^{-5} M)	55.8 ± 0.4	1.0×10^{-6} to 1.0×10^{-1}	0.9984
PVC + ionophore [b]	ClO_4^-(10^{-4} M)	56.7 ± 0.2	1.0×10^{-6} to 1.0×10^{-1}	0.9955
PVC + ionophore [b]	ClO_4^- (10^{-4} M) + ionophore (10^{-5} M)	52.2 ± 0.2	1.0×10^{-6} to 1.0×10^{-1}	0.9949

a: PVC (wt%):51.55; DBP (wt%):44.67; MTOAC (wt%):3.78.

b: PVC (wt%):49.36; DBP (wt%):42.90; MTOAC (wt%):3.62 ; Ionophore (wt%):4.12, $Ni(DBM)_2$.

Experimental conditions: Perchlorate concentration = 10^{-8} to 0.1 M; Temperature = 21 ~ 23 ^oC; pH = 5 ~7; Reference electrode = SCE

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Table S2. Chemical composition of water samples studied

	Cations (meq/L)								Anions (meq/L)				
Samples	pH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cu^{2+}	Fe^{2+}	Σ	HCO_3^{-}	SO_4^{2-}	Cl^{-}	NO_3^{-}	Σ
Creek Water	6.60	2.74	1.05	4.11	0.06	-	-	7.96	2.92	0.53	4.50	0.07	8.02
Rain Water	5.88	0.03	-	0.02	-	-	-	0.05	0.09	0.07	0.08	0.05	0.29
Tap Water	6.27	2.28	1.16	0.78	0.07	0.03	-	4.32	1.75	0.84	1.27	0.34	4.20