Development of Thiocyanate-Selective Membrane Electrodes by the Sol–Gel Method

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To prepare thiocyanate-selective chemical sensors, a sol–gel-based matrix was employed as a host membrane for the encapsulation of a sensing material. Tricaprylylmethylammonium thiocyanate (Aliquat336-SCN) was used as the dissociated ion-exchanger type sensing ionophore. Both 3-isocyanatopropyl-triethoxysilane and 1,4-butanediol were used for appropriate precursor preparation. Under acidic conditions, the sol precursor slowly gelled to yield a film in which the thiocyanate ionophore, Aliquat336-SCN, was encapsulated. Electrochemical responses of the potentiometric sensors were compared to those of traditional poly(vinyl chloride) (PVC) membrane electrodes prepared using the same ionophore. On the 7th working day, the average response slope toward thiocyanate was approximately 56.3 mV decade⁻¹ in the concentration range 10^{-4.5} M to 5 × 10⁻¹ M at 20°C. Selectivity toward thiocyanate over lipophilic anions such as perchlorate and salicylate was considerably improved. The results exhibit a clear tendency that deviates from the Hofmeister selectivity pattern which would be observed in a membrane electrode made of Aliquat336-SCN type salt. The potentiometric selectivity coefficients, as measured in a 0.05 M 2-morpholinoethanesulfonic acid monohydrate buffer, pH 5.5, were $\log k^{\text{pot}}_{\text{thiocyanate, chloride}} = -2.3$, $\log k^{\text{pot}}_{\text{thiocyanate, salicylate}} = -0.6$, and $\log k^{\text{pot}}_{\text{thiocyanate, perchlorate}} = -0.1$. The optimized membrane sensors were employed for the flow-injection measurement of thiocyanate levels in saliva samples from both smokers and nonsmokers. The membrane sensors exhibited a fairly good correlation with the traditional colorimetric method ($n = 23$; sensors = 0.84 (colorimetric) + 0.13; $R^2 = 0.97$).

Keywords: Thiocyanate-selective electrode, Aliquat336-SCN, Sol–gel encapsulation, Saliva

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