TECHNICAL NOTE

Use of bromide and thiocyanate ion-sensitive electrodes in the presence of quaternary ammonium ions

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We have been trying to use ion-selective electrodes to measure the concentrations of bromide and thiocyanate ions in aqeuous solutions of quaternary ammonium salts, typically tetrabutyl ammonium bromide and thiocyanate. The relevant electrodes are solid state and consist of silver sulphide plus silver bromide and thiocyanate respectively.

Typical commercially available electrodes gave excellent calibration curves with standard KBr/$NaNO_3$ and KSCN/$NaNO_3$ solutions, the Nernst equation being closely followed. With quaternary ammonium salts, however, anomalous readings were obtained and the response time of the electrodes rose from tens of seconds to tens of minutes and sometimes to hours. In several cases, equilibrium was not reached and there was long term drift in the e.m.f.

If the electrode was then washed and reimmersed in standard solutions, the anomalies and slow response times persisted. We were able to restore the electrodes to working order by polishing them with powdered alumina but quaternary ammonium compounds again fouled them.

The problem could be due to physical or chemical effects. Quaternary ammonium salts share some of the properties of cationic detergents and the cations might well adsorb strongly onto surfaces containing bromide and thiocyanate ions. Alternatively, chemical interactions between silver in the electrode and quaternary ammonium ions might occur. Silver is known to form complexes with nitrogen compounds and these might be insoluble and 'block' the electrode or they might be soluble and disturb the delicate solubility product balance on which the ion-selective electrode depends.

Whichever explanation holds, we think it worthwhile to report the apparent interference of quaternary ammonium cations with the operation of bromide and thiocyanate ion-selective electrodes.

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