DETERMINATION OF pH IN HIGH IONIC STRENGTH HCl SOLUTIONS USING A GLASS ELECTRODE

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Accurate determination of the activity of H^+ or pH in high ionic strength solutions is important for the understanding of thermodynamics and kinetics of reactions involved in mineral chemistry[1]. Although the glasss electrode is the most convenient and versatile electrode for pH measurements, its applicability in high ionic strength solutions remains questionable due to the uncertainty in corrections for the liquid junction potentials (EJ) and "acid error"[2]. This paper reports the measured pH in 0.001 - 6 mol dm^{-3} HCl solutions at 25°C using a glass - Ag/AgCl combined electrode and a solution of saturated KCl as the salt bridge. The difference between pH(GE) based on the glass electrode and pH(HE) based on the hydrogen electrode [1,3], which may be related to the "acid error", rarely exceeds 0.08 of a pH unit even in highly concentrated HCl solutions. There is a reasonable agreement between pH(GE), and pH(AF) based on acidity functions[4] and pH(EDH) based on the extended Debye-Huckel theory. This confirms the validity of EJ corrections based on the Henderson equation and the success of the glass electrode. However, the disagreement between pH(GE) and pH(AF) at HCl concentration > 4.0 mol sm^{-3} shows the non-validity of EJ corrections in extremely high ionic strength solutions.

References:

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