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GUIDELINES FOR POTENTIOMETRIC MEASUREMENTS IN SUSPENSIONS PART B. GUIDELINES FOR PRACTICAL pH MEASUREMENTS IN SOIL SUSPENSION

(IUPAC Recommendations 2006)

Prepared for publication by

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Guidelines for potentiometric measurements in suspensions

Part B. Guidelines for practical pH measurements in soil suspensions

(IUPAC Recommendations 2006)

Abstract: The measured cell potentials for suspension potentiometric cells have been interpreted and explained by a detailed analysis of the schemes for these cells [“Guidelines for potentiometric measurements in suspensions. Part A. The suspension effect (IUPAC Technical Report)”, *Pure Appl. Chem.* **79**, 67 (2007)]. Some former disagreements amongst investigations have been clarified. A new unambiguous operational definition of the suspension effect (SE) is presented. It is defined as the difference in cell potential for two suspension potentiometric cells, one with both electrodes in the separated equilibrium solution (eqs) and the other with both electrodes in the sediment or suspension. This potential difference is the sum of the change in the indicator electrode (IE) potential and the change in the liquid junction potential of the reference electrode (RE), when the electrodes are used for measurement, once in the sediment of the suspension and then in its eqs.

Keywords: operational definition of suspension effect; suspension effect; pH; suspension potentiometric cell; IUPAC Analytical Chemistry Division; pIon; boundary potential; mixed potential; soil pH; anomalous liquid junction potential.

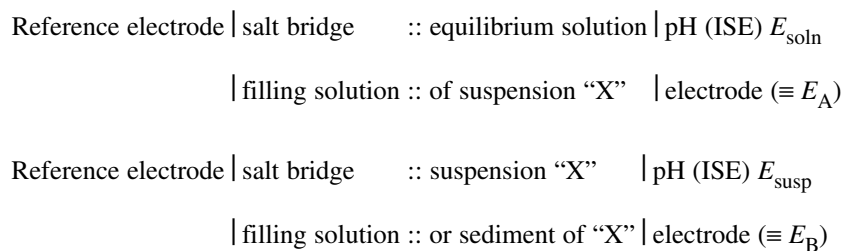
1. INTRODUCTION: RECOMMENDED DEFINITION OF THE SUSPENSION EFFECT (RECOMMENDED TERMINOLOGY FOR pH (pION) MEASUREMENT IN SUSPENSIONS)

Two disputable definitions of the suspension effect (SE) can be found in current IUPAC recommendations [1,2], both erroneously assuming that a boundary potential is the essential part of the SE. The existence of such a potential is not supported by experimental evidence [9,14]. The findings presented in “Guidelines for potentiometric measurements in suspensions. Part A. The suspension effect (IUPAC Technical Report)” [5] regarding the origin and interpretation of the SE require modification of the definition of the SE.

2. RECOMMENDATION FOR THE OPERATIONAL DEFINITION OF THE SUSPENSION EFFECT

Considering the IUPAC Recommendations 2002 of pH measurement [6] and the analysis of the schemes of suspension potentiometric cells, presented in “Guidelines for potentiometric measurements in suspensions: Part A. The suspension effect (IUPAC Technical Report)” [5], the *operational definition of the SE* at any temperature and pressure is:

Potential difference $\Delta E_{SE} = E_{\text{susp}} - E_{\text{soln}}$ of two suspension cells, presented in the following cell diagrams and measured both under the same conditions of temperature and pressure and with the same indicator electrode (IE) and reference electrode (RE) (with salt-bridge filling solution):



From ΔE_{SE} , the SE values can be calculated and expressed as $\Delta\text{pH}(\text{SE})$, as was the case in the first definition of the SE [3], or as $\Delta\text{pIon}(\text{SE})$, when any ion-selective indicator electrode (ISE) is used for the potentiometric measurements in suspensions.

The cell containing the equilibrium solution (eqs) of the suspension (original or modified) gives the best-defined E_{cell} (and the corresponding pH value) obtainable with any suspension potentiometric cell [13]. Thus, it is the appropriate reference potentiometric cell for comparison of results obtained by modified methods for potentiometric measurements in suspensions.

When the SE determinations on different suspensions are intended for the comparison of characteristics of these suspensions, saturated KCl solution is the recommended salt-bridge filling solution. The separation of the suspension into its sediment and its clear eqs can be performed by any suitable separation method.

3. INTERPRETATION OF THE SUSPENSION EFFECT

The interpretation of the SE, supported by analysis of schemes for the suspension potentiometric cells with the aid of which the SE is defined, gives consideration to the previous study of numerous SE researchers and above all to the more recent experimental findings on SE.

As a result of the present analysis, the SE is considered as the sum of two independent potential changes that arise when the electrodes are transferred from the eqs to the suspension. The first potential change is the change of the IE potential (*SE of the first kind*). The second potential change is the change of the liquid junction potential when the RE makes contact with the suspension (*SE of the second kind*). Experiments indicate that there is no measurable boundary potential between the sediment and the separated eqs. Therefore, there is no boundary (or Donnan) contribution to the SE.

The suspension effect of the first kind (SE 1) is caused by the transformation of the pH electrode (or ISE) from being a single electrode when immersed in the eqs of a suspension into a multiple electrode when immersed in a suspension or sediment (the *cause* of SE 1). This transformation is the consequence of the overlapping of the electrode diffuse double layer with the particle diffuse double layers. The overlapping happens when particles make intimate contact with the electrode surface [7]. The primarily Nernst electrode potential formed in the eqs changes to an irreversible mixed (steady-state) electrode potential when the electrode is introduced into the appropriate suspension or sediment (the *nature* of SE 1). This mixed potential is mostly constant during practical potentiometric measurements. The SE 1 cannot be eliminated in potentiometric measurements where the IE is in contact with the suspension.

The *suspension effect of the second kind* (SE 2) arises from the diffusion or outflow of the (saturated KCl) filling solution from the salt bridge of the RE into the suspension or sediment (the *cause* of SE 2) [8]. When KCl solution contacts the dispersed charged particles, ion exchange with the particle counterions or a change of ion arrangement around the particles may occur. This can annul the ability of the KCl solution to moderate the liquid junction potential of the RE and may increase it enormously. The effect is caused by the K^+/Cl^- diffusion front of the KCl solution being replaced by a H^+/Cl^- diffusion front, which results in a larger diffusion potential. These effects result as an appearance of an anomalous liquid junction potential (the *nature* of SE 2). The SE 2 represents a systematic error of the suspension measurement by potentiometric methods. The SE 2 can be eliminated by an RE that is

equipped with a double salt bridge; that is, an RE having the suspension-contacting part filled with the eqs of the measured suspension or by an equivalent arrangement.

More explanatory information on the above themes is obtainable in refs. [5–9].

4. GLOSSARY OF TERMS USED IN THESE RECOMMENDATIONS

This Glossary presents recommended terminology related to the SE.

suspension of solid charged particles

Dispersion of solid electrically charged particles, commonly larger in size range than colloidal particles (of approximate diameter range 1–1000 nm) (dispersed phase), in water or an aqueous solution (continuous, liquid phase).

Note: Suspension can be a uniform system, i.e., an optically equable (uniform) mixture of both phases, or a combined system in which a part of the liquid phase of the equilibrated suspension eqs is separated from the rest of the suspension. By sedimentation of particles, a concentrated phase (sediment) can be formed, in which particles are still surrounded by the intrinsic liquid phase, the eqs. Both parts remain in physical and electrical contact.

suspension potentiometric cell

Galvanic cell containing, as its essential component, a uniform or combined suspension or one of its separated parts alone, the eqs or sediment.

anomalous liquid junction potential

Electrochemical potential that arises at the RE–measurement solution interface when, during a potentiometric measurement, the filling solution of the salt bridge of the RE contacts the charged particles of a suspension.

Note: The value of the anomalous liquid junction potential can exceed significantly the commonly occurring liquid junction potential, depending on the suspension species and the concentration of the filling solution. The contact between the electrolyte in the RE (or its salt bridge) and the charged particles can change the ion arrangement around the particles and modify the approximate equality of the ion transport numbers in the electrolyte diffusion front (e.g., by ion exchange of H^+ or OH^-); this ion exchange will diminish the suppression of the diffusion potential.

suspension effect

Effect arising from presence of a *suspension* in an electrochemical cell containing an IE and an RE. Operationally, the SE has two definitions, depending on the particle concentration of the suspension:

1. SE' (general): Potential difference $\Delta E_{SE'} = E_{B'} - E_A$ of two electrochemical cells A and B', where the IE and RE are first placed in the undispersed suspension of a specified particle concentration (cell B', potential $E_{B'}$) and then in the eqs of this suspension (cell A, potential E_A).
2. SE (special): Potential difference $\Delta E_{SE} = E_B - E_A$ of two electrochemical cells A and B, where the IE and RE are first placed in the eqs of the sedimented suspension (cell A, potential E_A) and then in the sediment itself (cell B, potential E_B , where the particle concentration is better defined and gives more reproducible results).

(Both forms replace the original definition of the SE [3]: the difference in pH in suspensions containing different concentrations of the same particles, measured by a potentiometric method.)

Note 1: The SE is the sum of two potential differences:

1. The SE of the first kind, SE 1, which arises at the IE and is the difference between the mixed potential generated in the sediment and the electrode potential generated in the eqs, and
2. The SE of the second kind, SE 2, which arises at the interface between the salt bridge of the RE and the suspension. It is the difference between the liquid junction potential of the RE when placed in the sediment and in the eqs.

Note 2: The cause of SE 1 is the intimate contact of the electrode surface with the diffuse double layers of the particle. Its nature is an irreversible mixed (steady-state) potential.

The cause of SE 2 is the outflow of the salt-bridge filling solution from the RE and the interaction of this electrolyte with particles with which some ion exchange may occur. The nature of SE 2 is the resulting abnormal liquid junction potential, possibly of a very high value.

Note 3: The potential differences mentioned can also be given as the corresponding pH (or pIon) values.

pIon

General mathematical expression form of any ion X activity: $p(\text{ion X}) = pX = -\lg a_X = -\lg (m_X \gamma_X/m^\circ)$, analogously to $pH = -\lg a_H = -\lg (m_H \gamma_H/m^\circ)$.

Note: Practical pIon measurement with the proper reversible ISE can be carried out by means of a galvanic cell, composed correspondently to cell V, published in “Measurements of pH (IUPAC Recommendations 2002)” [6, p. 2187]. The accuracy and uncertainty of results obtained with ISEs depend analogously as in pH measurement for all on validity of standard solutions used, if the common guidelines for potentiometric measurement are taken in account.

The term “pIon” is used mainly in the literature, oriented to the practical routine work, e.g., ref. [16].

suspension (soil) pH

Readings on a pH-meter scale obtained for a suspension of soil (in water or electrolyte) by any method for potentiometric pH measurement, performed in a manner analogous to the pH measurement in solutions.

Note: Most of the reported “suspension (soil) pH” values have no known quantitative connection with the hydrogen ion activity in suspensions; nevertheless, they are more or less repeatable characteristic values of the measured suspensions.

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