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Glass Electrode Half-cells for Measuring Unified pH in Water-organic Solvent Mixtures

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Summary:

Unified pH enables to compare acidities between any given solvent or mixtures thereof. So far only metal solid contact glass electrode half-cells have been used. Three commercial, conventional glass electrode half-cells with inner liquid filling were used to investigate the dependence of the unified pH scale on the different electrodes.

Keywords: unified pH, absolute acidity, glass electrodes, half-cells, organic solvents

Introduction

pH is an important factor in many processes. pH measurement in non-aqueous solvents has several problems and interpretation of obtained pH values is complicated. Because of the significant dependence of the proton activity on the solvent, every medium has its own pH scale. Thus, pH values measured in different solvents cannot be compared. Therefore, it is impossible to differentiate acidities of solutions made with different solvents. Unified pH [1] allows direct comparison of acidities in all media and is measured potentiometrically [2] by measuring directly the potential between two glass electrode half-cells.

The unified acidity scale uses an ideal proton gas as a theoretical, but universal reference point and its absolute chemical standard potential is set to zero. In solutions, the chemical potential of the proton is reduced by interaction with its environment which defines the pH scale of a specific solution [1]. However, the scales of different solutions can be related to each other through their common reference to the proton gas. Thus, their respective acidities can be compared if the pH values are transferred to this common, unified pH scale.

Until now all the unified acidities have been measured with metal solid contact glass electrode half-cells [3]. These electrodes give stable and reproducible signals in non-aqueous solvents and their mixtures with water. From a metrological perspective it is desirable that a measurand does not depend on the instrument used to measure it. Therefore, we investigated the dependence of unified pH measurement results on various kinds of electrodes that are designed for non-aqueous solutions and that are commonly available.

Method

The unified pH was measured in aqueous mixtures of ethanol. Aqueous standard buffers with pH 4.01, 7.00 and 9.00 were used for validation. The cell used (1) was like the one used in [2], however, a slightly different, because an almost ideal ionic liquid (triethylpentylammonium bis(trifluoromethylsulfonyl)imide, $[N_{2225}][NTf_2]$) [4-5] was used to eliminate the liquid junction potential.

$$\mathrm{GE_1} \mid \mathrm{Solution_1} \mid [\mathrm{N_{2225}}][\mathrm{NTf_2}] \mid \mathrm{Solution_2} \mid \mathrm{GE_2} \quad (1)$$

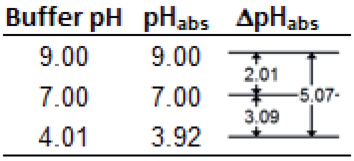
The potential ΔE measured between two glass electrodes (GE) was converted into ΔpH with eq (2):

$$\Delta \mathrm{pH} = \frac{\Delta E + Int_{\mathrm{RE}} - Int_{\mathrm{WE}}}{slope_{\mathrm{average}}} \quad (2)$$

Where Int_{RE} and Int_{WE} are the intercepts of the reference (GE_1) and working electrode (GE_2), respectively, and $slope_{\mathrm{average}}$ is the average slope of the two electrodes. Slopes and intercepts are obtained when the potential of an electrode is measured against a reference electrode in aqueous standard buffers.

A so-called ladder approach [2] is used to assign absolute pH values ($\mathrm{pH_{abs}}$) to the measured solutions based on measured ΔpH values ($\Delta\mathrm{pH_{abs}}$) between different combinations of the solutions in the cell. The $\mathrm{pH_{abs}}$ values are calculated by applying a least-squares minimization technique to the measured $\Delta\mathrm{pH_{abs}}$ values. The consistency standard deviation of the pH ladder is used to evaluate the mismatch between the measured ΔpH_{abs} and assigned pH_{abs} values. An example of such a ladder is shown in Fig. 1, which shows the measured ΔpH_{abs} values of typical aqueous standard buffers (borate, phosphate and phtalate), the assigned pH_{abs} values and, for comparison, the pH values known from primary pH measurements.

Metal solid contact glass electrodes from Izmeritelnaya tekhnika and glass electrode half-cells with inner liquid filling from Horiba, Metrohm and Mettler-Toledo were investigated. Two cells of each manufacturer were used. All measurements were done at 25 °C.



Buffer pH	pH_{abs}
9.00	9.00
7.00	7.00
4.01	3.92

Fig. 1. pH ladder with aqueous standard buffers. Electrodes from Horiba. Buffer pH 7 was fixed.

Results

The consistency standard deviation, *s*, is the main characteristic to evaluate the suitability of electrodes. It is affected both by the reproducibility and the stability of the signal. All electrodes give acceptable results in standard aqueous buffers. However, the results from water-organic solvent mixtures are not as good. Differences in the assigned pH_{abs} values can be up to one pH unit.

Tab. 1: pH_{abs} results with water-ethanol mixtures. Percentages given in mass. Buffers pH 7.00 and 4.01 were fixed.

Electrode	50% EtOH	80% EtOH	*s*
Metrohm 6.0150.100	7.78	8.87	0.10
Horiba Scientific/Laqua Model 1076A-10C	7.38	9.01	0.16
Mettler-Toledo DG300-SC	6.95	8.16	0.13
Izmeritelnaya tekhnika EST-0601	7.44	9.18	0.07

Although the electrodes are meant for non-aqueous solvents, they give quite unstable reading, when used in the investigated cell (1). The drift can be more than 30 mV/h depending on the pair of solvents measured. The higher the content of organic solvent, the less stable is the reading. An example of the stability of the potential is shown in Fig. 2.

The metal contact glass electrodes perform better compared to the electrodes with inner filling. Work is still in progress to evaluate the cause of inconsistency between the different electrodes and to improve the measurement procedure.

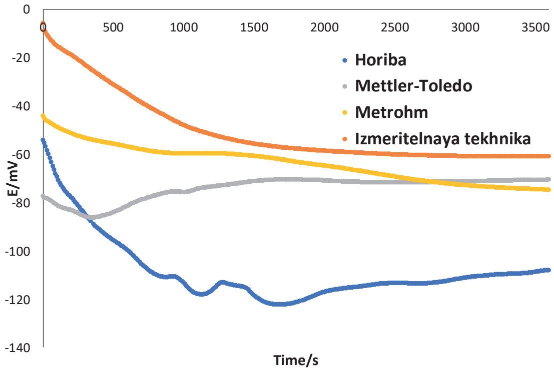


Fig. 2. Stability of potential measured between 80 m% ethanol and 50 m% ethanol during 1 h.

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