Publishable Summary for 17FUN09 UniphHied
Realisation of a Unified pH Scale

Overview

To date, it is impossible to compare pH values of solutions made in different solvents. This situation is untenable, since it causes confusion and inaccuracies in many fields, extending far beyond the specific field of acid-base chemistry, to almost all spheres of life. The purpose of this project is to overcome this situation by putting the new theoretical concept of a unified pH_{abs} scale on a metrologically well-founded basis into practice. The project results will ensure that pH measurement systems are available to industry and academia for accurate pH testing in a wide variety of media.

Need

The pH of solutions is probably the most prominent chemical concept widely utilised outside the field of chemistry. It is used in a near uncountable number of areas, *e.g.,* medicine and life sciences, biology, environmental science, agrology, marine sciences, meteorology, material sciences, corrosion science, energy related sciences, etc. It plays an important role in virtually all material related processes, in their production (*e.g.,* processing metals, paper, plastics, glasses, etc.) as well as in their reprocessing (domestic and industrial wastewater, extraction of solid wastes, etc.). Accurate analysis and monitoring of pH values is therefore an extremely important task in a wide variety of technologies. This variety entails a diversity of media in which those processes occur, *i.e.,* different solvents, solvent mixtures, and dispersions. For basic thermodynamic reasons, valid comparability of pH values in different media has been impossible for a long time, even on the theoretical level. As a result, several pH scales exist in parallel, loosely correlated to each other, without the possibility of converting one scale into the other to the necessary level of accuracy. It is known that there are potentially 1.5 million pH electrodes used in industrial applications today, of which a number (10 % - 20%) are placed in solvent mixtures which are not suitable for the current offerings and lead to rapid failures.
In 2010, the unified acidity (pH_{abs}) concept was introduced to overcome this untenable situation, enabling comparability of pH values between all phases, whether they are gaseous, liquid, or solid. Although conceptually excellent, putting this concept into practical use has proved tremendously difficult and has not yet been fully achieved. In order to be practically usable the knowledge of physicochemical quantities is required, access to which is not straightforward. Additionally, suitable measurement and calibration procedures are required, all of which still need to be developed.

Objectives

This project concerns the practical realisation of the theoretical concept of pH_{abs}. This includes the determination of the mentioned quantities, as well as the standardisation of the measurement and calibration processes of pH_{abs}. The major objectives laid out for this project are:

1. To develop and validate a reliable and universally applicable measurement procedure, that enables the measurement of pH_{abs} (expressed relative to the aqueous scale, as $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$-values) in non-aqueous and mixed solvents, colloids, etc., thereby enabling their acidities to be compared to the conventional aqueous pH scale. The target combined standard uncertainties to be 0.15 pH_{abs} in "good" (mixed aqueous, alcohols, etc.) and 0.25 pH_{abs} in "difficult" (colloids, aprotic, etc.) systems.
2. To create a reliable method for the experimental or computational evaluation of the liquid junction potential between aqueous and non-aqueous solutions where the bridge electrolyte is an Ionic Liquid, allowing correction of results from, for example, a glass electrode pH measurement setup calibrated with aqueous standards measuring non-aqueous samples.
3. To develop a coherent and validated suite of calibration standards (including procedure and sensor) for standardising routine measurement systems in terms of pH_{abs} values for a wide variety of media (e.g., industrial mixtures, soils/waters, food products, biomaterials).
4. Based on the outcome of the project, to contribute to the international specifications for bioethanol quality EN 15490 (e.g., by assigning values to existing certified reference materials) and other relevant

standards development organisations, and to disseminate the findings to the European measurement infrastructure.

Progress beyond the state of the art

Depending on individual requirements and technical possibilities, several pH scales have been developed over the last century. However, these scales suffer as a result of their incompatibility, *i.e.,* a certain value in one scale cannot be converted to a value on another scale with acceptable accuracy, typically below 0.05 pH_{abs}. Therefore, this project will establish a practical method of measuring pH of any medium on a universal scale (termed here as pH_{abs}), which will make pH values comparable between solvents/media. A procedure for pH_{abs} measurement will be developed on the basis of differential potentiometric techniques with electrodes specially designed to work in non-aqueous solutions, as well an "ideal" ionic liquid salt bridge composition. The use of such a system will enable the quantification of liquid junction potentials (LJPs), which arise from the different physicochemical properties of the solvents forming the junction and are currently difficult to evaluate and control.

Typically, 70 % of the cost of running commercial pH sensors is taken by the labour required to calibrate and maintain current commercial offerings.

This project will develop a novel solid state redox pH sensor to enable routine measurement of pH_{abs} with no need for sophisticated equipment, suitable for direct use by field practitioners. It will also provide guidelines dedicated to implementing specific approaches for practical usage of the unified pH scale by practicing chromatographers. This represents substantial progress and goes well beyond the results provided in the BIOREMA project (2011-2014) and EMRP ENG09 project (2010-2013) to reach a reference metrology level for pH measurement in complex media, such as mixed aqueous or organic solvents.

Results

The project expects to achieve a number of key outputs including:

Objective 1: Universally applicable procedure for measuring pH_{abs}

- A reliable and robust system allowing implementation of the pH_{abs} concept at National Metrology Institutes (NMIs) level
- A guideline on measuring $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$-values for several mobile phases
- Suitable electrode types for the purpose of pH_{abs} measurements in water-organic solvent mixtures with quantified performance characteristics
- A general procedure for pH_{abs} measurement on the basis of differential potentiometry with target combined standard uncertainties of 0.15 pH_{abs} in "good" (mixed aqueous, alcohols, etc.) and 0.25 pH_{abs} in "difficult" (colloids, aprotic, etc.) systems
- An interlaboratory comparison to evaluate the performances of pH_{abs} measurement procedure and propose recommendations for further improvements of the method.
- A recommendation for the pH measurement of ethanol-containing products will be developed for the first time including suggestions to improve the comparability of acidity values for water-ethanol mixtures containing a mass fraction of ethanol close to 1. This procedure will enable users to estimate, for example, the acidity strength of bioethanol used as a blending for petrol (based on EN 15490).

Objective 2: Method for evaluation of the LJP between aqueous and non-aqueous solutions

- A new salt bridge composed of a room temperature ionic liquid in several water-organic solvent mixtures namely water-methanol, water-ethanol and water-acetonitrile.
- A protocol for evaluating LJP if the bridge electrolyte is an ionic liquid. This will be used to raise awareness of pH measurement bodies (industry, analytical chemistry laboratories) towards the necessity to consider the LJP for pH determination.
- Guideline documents to facilitate implementation of the procedure by any laboratory in the field

Objective 3: Calibration standards for routine measurement of pH_{abs}

- Traceability of pH_{abs} to pH aqueous buffer solutions established. The obtained pH_{abs} values will be rigorously linked with the aqueous pH scale, yielding $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$ that is equal to the conventional aqueous pH-value.
- A demonstration of the advantages of using the $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$ values to improve comparability of acidity values measured in ethanol products as well as the benefits of measuring $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$ values for LC and/or MS analytical techniques
- A novel solid state redox pH sensor that can determine $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$ values for non-ideal solutions

Impact

Impact on industrial and other user communities

The project strives towards a reliable and practical method of measuring and expressing acidity of any medium on a universal scale (termed here as $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$-values). Manufacturers of pH meters will have a reliable means to characterise and benchmark their devices in solutions other than aqueous, since they can directly compare the results of different types of devices in various matrices using the unified pH_{abs} scale as a root of traceability. Users of liquid chromatography and its derivative methods (including, most importantly, HPLC) will benefit from using the pH_{abs} scale to allow a better adjustment of mobile phase pH, leading to higher accuracies in concentration determination and higher efficiency in separation processes. Through IUPAC (International Union of Pure and Applied Chemistry) and National and European Standardisation Bodies, implementation of the new analytical method will be facilitated, for example, to improve water quality assessment through acidity comparison of different LC mobile phases.

The sensor device produced within the project lifetime will demonstrate the maturity of the concept exploring the possibility for implementation at wider scale. In this respect the produced sensor will be tested by an academic stakeholder in food/beverage matrices.

In the longer term, routine laboratories will be able to measure $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$ whilst – very importantly – using their standard pH measurement equipment (i.e., there will be no need to install sophisticated differential potentiometry setups). This will be possible once measurement standards (reference materials), accurately characterised in terms of $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$, become available.

Impact on the metrology and scientific communities

The work in the project will have a strong metrological impact. The outputs of the project will allow NMIs and designated institutes to develop new Calibration and Measurement Capabilities (CMCs). Provision of a measurement procedure and a coherent system of calibration standards in terms of pH_{abs} will provide the foundation for certification of reference materials (CRMs), which, once available, can be used by routine laboratories for measurement of non-aqueous solutions as above.

The project will also create impact through publications of the work in high-ranking peer-reviewed journals. pH measurements as proposed in the project are based on electrochemical techniques concerning the redox system H^+/H_2. The comparability of any redox system in different solvents suffers from unknown LJP values. Thus, the determination and provision of LJP values determined in this project can be used by electrochemists in general, dealing with non-aqueous media of any kind, and hence, for a multitude of topics, *e.g.,* in the fields of batteries or corrosion. Furthermore, stimulation in the field of single-ion thermodynamics in expected, hence the topic is also relevant to basic research in thermochemistry.

Research in the project will be conducted in close relationship with IUPAC, which is the global organisation that provides objective scientific expertise and develops the essential tools for the application and communication of chemical knowledge for the benefit of humankind and the world. The work undertaken in this project will be incorporated into the efforts already started by IUPAC to address pH assessment in non-aqueous and mixed solvents.

Impact on relevant standards

Quality-assuring bioethanol when it is used as fuel is a key requirement of the trade, regulation, and usage of the material. Thus, reliable analytical protocols for pH_{abs} measurements of ethanol, based on differential potentiometry techniques will be provided, contributing significantly to the improvement of the comparability of acidity values measured using the EN15490 standard method. The project will also support active participation in the metrological activities of key international and European committees: BIPM/CCQM/EAWG, and EURAMET TC-MC.

Longer-term economic, social and environmental impacts

Since pH is possibly one of the most important chemical parameters in science, technology, environment and health, the project´s broader impact is potentially enormous, yet difficult to quantify. It is clear that any uptake of the project´s outcomes by any fields regarding pH values or redox values in non-aqueous (but also aqueous and mixed-aqueous) solutions will also lead to further development within these fields. Thus, we reasonably expect beneficial effects for European industry as a whole, but also for the public sector. The measurement standards of pH_{abs} and/or $\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$-values can be embedded into the European measurement infrastructure, thereby underpinning the whole area at an EU level.

The developments in the project will enable more efficient process control in the EU chemical industry, which is a large branch of the European economy, employing 1.2 million workers and contributing €519 billion annually.
The project will be a vector of innovation for the development of the next generation of electrodes (e.g., “lab on chip”). Such electrodes would be useful in the biomedical field, especially for cancer chemotherapy, and will contribute towards the reduction of the cost of cancer treatment.
Europe is a key player in addressing environmental sustainability and the global climate challenge. This project would contribute to a further understanding of the chemistry of water bodies (particularly sea water, a highly important ecological system). Extensive and continuing CO_2 absorption by seawater causes acidification, evidenced by a reduction in pH and changes in the ocean carbonate chemistry. Serious discrepancies have been noticed in established trends in seawater acidity due to the existence of several measurands for the same quantity. Establishment of the unified pH concept and pH_{abs} measurement procedures would enable the expression of seawater acidity on a comparable scale, hence increasing our understanding of processes in seawater media.
Potential allergenicity of newly introduced proteins in genetically engineered foods has become an important evaluation issue. The digestion process used to evaluate the foods’ allergy risk is monitored by analytical techniques that are highly sensitive to pH control. The project outcomes would enable the establishment of standardised assay conditions so that direct comparison of results from different laboratories can be made. Hence, the project will help generate the evidence needed to inform the public and develop policy for public health protection.

Project start date and duration:	01 May 2018 (36 Months)	
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