

ELECTROCHEMICAL ACIDITY FUNCTIONS

Jiří JANATA^{a,*} and Petr ZUMAN^b^a School of Chemistry and Biochemistry, Georgia Institute of Technology,
Atlanta, GA 30332-0400, USA; e-mail: jiri.janata@chemistry.gatech.edu^b Department of Chemistry, Clarkson Institute of Technology,
Potsdam, NY 13699-5810, USA

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Dedicated to the memory of Professor Jaroslav Heyrovský on the occasion of the 50th anniversary of the Nobel Prize for polarography.

Experimental realization of a reference potential for potentiometric measurements in non-ideal media is discussed. A liquid junction-free reference potential is realized at a dropping mercury electrode, using the standard potential of the metallocene redox couple. This approach is particularly suitable for determination of acidity functions that are seamlessly anchored to aqueous standard buffers.

Keywords: Acidity functions; Metallocene assumption; Non-ideal reaction media; Polarographic reference electrode; DC polarography; Electrochemistry.

Measurement of activity of the most ubiquitous and the most important ion, the hydrated proton, known as the hydronium ion, is the subject of great interest in many areas of physical chemistry. It is commonly done by spectroscopic determination of acidity functions. Although there are many different acidity functions, depending on the type of the indicator used and on the nature of the acid or base used for their measurement, they are invariably anchored to the common standard state, aqueous buffer solutions, in which the hydrogen ion activity is electrochemically determined with a glass electrode¹. It should be stressed that the operational hydrogen scale is only empirical, based on the measurement of cell voltage in arbitrarily selected buffers. Solutions of extreme activities of solvated hydrogen or hydroxyl ion belong to the category of non-ideal reaction media, in which the limiting Debye–Hückel approximation is no longer valid. Non-ideal media are represented by mixed organic–aqueous systems (Ritchie), by concentrated solutions of electrolytes and by solutions involving room-

temperature ionic liquids. Thus, values between $-\log a_{\text{H}^+} = -10$ and $+26$ have been reported in various aqueous–organic systems. The common practical approach to quantifying extreme acidity or basicity has been through the Hammett acidity functions, based on spectroscopic determination of *concentrations* of protonated and unprotonated forms of a suitable set of Hammett indicators, under the assumption that the ratio of their activity coefficients (Eq. (1)) remains constant. Because spectroscopic measurements determine concentrations rather than activities of various solvatomers and because the Gibbs free energies of solvation of different families of indicators and acids (or bases) can be vastly different, there are many different acidity functions for otherwise the same compositions of the reaction medium².

The activity of the hydrogen ion written in complete form of the association equilibrium of the indicator is clearly affected by the changes of the ratio of the activity coefficients of the two forms of the indicator pair: $\text{A} + \text{H}^+ = \text{AH}^+$. Thus,

$$-\log a_{\text{H}^+} = \text{p}K + \log C_{\text{A}}/C_{\text{AH}^+} + \log f_{\text{A}}/f_{\text{AH}^+}. \quad (1)$$

When this equilibrium is considered in purely aqueous solution water is always in such a large molar excess that its activity is constant and does not need to be taken into account. However, that is not the case for mixed aqueous–organic solvent media where water can be a minority component. In such case each species undergoes solvation by all solvent components and the situation becomes rapidly quite complex. A reasonable simplifying assumption can be made that only the hydration (i.e. solvation with water) of charged species is considered. Depending on the hydrophobicity of the indicator such simplification can be justified in most but not all cases. The hydration of the charged form of the indicator relative to the hydration of proton underscores one fundamental weakness in the Hammett indicator based approach. Thus, for the proton it is possible to write



where symbol W is used as abbreviation for water. The hydration equilibrium with cumulative equilibrium constant K_{H} is

$$K_{\text{H}} = \frac{a_{(\text{HW}_x^+)^+}}{a_{\text{H}^+} a_{\text{W}}^x}. \quad (2)$$

Likewise for the hydration of the protonated indicator AH^+ we have



with the corresponding hydration equilibrium constant

$$K_{\text{AH}} = \frac{a_{(\text{AHW}_y^+)}}{a_{\text{AH}^+} \cdot a_{\text{W}}^y}. \quad (3)$$

Combining these hydration equilibria for charged species with the association equilibrium constant for the indicator, taking the logarithm and rearranging, yields for general Hammett acidity function H_0

$$-\log a_{\text{HW}_x^+} = H_0 = \text{p}K + \log C_{\text{A}} / C_{(\text{AHW}_y^+)} + \log f_{\text{A}} / f_{(\text{AHW}_y^+)} - (x/y) \log a_{\text{W}}. \quad (4)$$

The first two terms on the right-hand side of Eq. (4) constitute the spectroscopically determined acidity function for a given indicator set. The ratio of the activity coefficients (in the third term) accounts for the variability of acidity functions among different indicator sets and among different media. This is a well-recognized limitation of the Hammett approach, which is usually circumvented by using the type of indicator that has approximately the same solvation properties as the species under study. Such matching of solvation energies is rarely possible.

The less recognized limitation reflects the role of the fourth term of Eq. (4). Because of the difference in the solvation numbers (and energies) of the indicator set and the hydronium ion it is not possible to compare different types of indicators and not even the same indicator going from one reaction medium to another. In other words, the fourth term causes the different water–organics mixtures to have vastly different acidities (or basicities) even for identical molar compositions of the base (or the acid). This is due to the fact that different organic solvents have different ability to form solvatomers. Since proton is the most strongly solvated ion, it can be argued that always $x \gg y$. It should be noted that no assumption has been made about the actual values of the solvation numbers x and y and that solvation number of the neutral form of the indicator is assumed to be invariable. This means that according to Eq. (4), decreasing concentration of water causes an increase in acidity (or basicity). In other words, when water becomes a minority component in the system it has a strongest effect on the activity of the ions that it solvates. This fact is often not recognized in the

studies of liquid|liquid interfaces, in which the organic phase invariably contains a small, but very important fraction of water, which then dominates the activities of the ions in that phase. The dominating effect of the "minority water" in organic phase is clearly visible in basicity functions shown in Fig. 2b. Furthermore, the use of Hammett acidity functions is often limited to aqueous solutions containing variable concentration of acid or base.

Electrochemical Determination of Acidity Functions

It is legitimate to ask why, in spite of such serious deficiencies, are the Hammett acidity functions so popular? The answer lies apparently in the fact that their spectroscopic determination is relatively easy. All that is needed is a set of chemically similar indicators with suitably spaced pK values. Nevertheless, it would be clearly desirable to define a universal scale of hydrogen (or hydroxide) ion activity that would be independent of the indicator and solvation effects and that would have an aqueous standard state. Our electrochemically determined acidity function based on behavior of a glass electrode would be such a scale. It would have its standard state defined by conventional aqueous buffers and would progress from there seamlessly to non-ideal media of extreme acidities. For such measurement to be done there is needed a liquid junction-free reference electrode and a reversible electrode that responds exclusively to hydronium ion. It has been noted that, when hydrated, a low asymmetry potential, low alkali ion error glass electrode functions well in completely non-aqueous media³. It is so because the hydrated surface layer at the glass electrode has a very high affinity to water and retains water even in pure organic solvents.

The operational definition of pH is based on comparison of voltages $E(X)$ and $E(S)$ of a cell comprising pH electrode (hydrogen or glass) and a standard reference electrode, such as calomel electrode connected to the solution via the liquid junction. The measurements are done in a standard buffer of arbitrarily defined activity of hydronium ion $a_H(S)$. The indices S and X refer to standard and solutions of unknown hydronium ion activity, respectively. Because the solvation states of the species that establish the interfacial potential of the indicator electrode are unknown the pH is simply defined as

$$pH(X) = pH(S) + (E_{\text{glass},X} - E_{\text{glass},S})F/2.303RT + (E_{j,X} - E_{j,S})F/2.303RT \quad (5)$$

The buffers used for this standardization are specified by international convention¹. An assumption built into this potentiometric procedure is the invariability of the liquid-junction potentials i.e. that $(E_{j,X} - E_{j,S}) = 0$. This assumption usually holds only for dilute aqueous solutions.

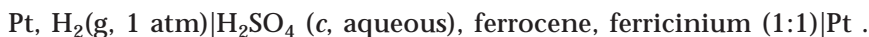
The information obtained from any potentiometric measurement is split equally between the potential of the indicator and the potential of the reference electrode. It is tacitly assumed that the potential of the latter is invariable. There is a disproportionately large volume of literature concerning the indicator electrode, but relatively little concerning the latter. It is the consequence of the fact that there is not much glamour in investigation and development of high-quality, reliable reference electrodes. Yet, the consequences of an ill-defined reference potential can be just as serious as the source of experimental artifacts produced by the faulty indicator electrode. Ironically, experimental errors due to the one, the other or both electrodes cannot be experimentally separated. It is so because a single electrode potential cannot be experimentally determined⁴.

The errors due to the variable or ill-defined reference electrode potential can be almost always attributed to the liquid junction. In this paper somewhat unusual realizations of reference potential shall be reported, in which the possible experimental error due to liquid junction is eliminated. The approach is suitable for electrochemical measurements of ion activities that are far from the "ideal region", particularly for variations of acidities in water-organic solvent mixtures. The liquid junction and its associated potential is the "evil" component of any potentiometric measurements in non-ideal media, such as mixed organic-aqueous solvents, solutions of high ionic strength or systems involving room-temperature ionic liquids. First of all, it must be realized that due to its nature, any liquid junction is a non-equilibrium element, because it involves a dissipative process, i.e. diffusion. That fact renders measurements of cell voltage involving liquid-junctions "non-equilibrium", despite the fact that they are done at zero cell current. Because of this, the junction is the most vulnerable component of any electrochemical measurement and contributes more than its fair share to the creation of experimental pitfalls. The problem becomes most acute when the junction connects two dissimilar solvents, e.g. in aqueous-organic solutions. Experimental errors amounting to several hundred millivolts can accrue if, e.g. aqueous reference electrode junction is used in an organic or mixed electrolyte and the salts used in the aqueous compartment of the reference electrode precipitate inside the junction. Although the focus of this paper is on measurement of hydronium ion activities, the methodology and experimental approach described here are equally

valid for determination of activities of other ions, for which ion-selective electrodes are available.

Experimental Approach

Some “extra-thermodynamic” assumptions always have to be made, if we attempt to determine a single electrode potential. The assumption of zero solvation energy change of the ferrocene/ferricenium redox couple has been proposed by Strehlow⁵. They used Pt electrode immersed in a 1:1 solution of ferrocene/ferricinium as a reference against which potential of the hydrogen electrode was measured in the cell represented as



Although conceptually correct, that arrangement had a serious experimental deficiency, namely the undefined ratio of the ferrocene/ferricinium redox couple. Other metallocene redox couples of Co, Ni, Ru, etc., have been used as internal reference potentials in several organo-electrochemical studies. The rationale and justification for this assumption is the delocalization of the excess charge density over the spherical surface of the metallocenium ion, which results in the minimum difference of the solvation energy between the neutral and the charged molecule. The difference has been calculated using the density functional theory (Polarized Continuum Model) for several organic solvents⁶. The stability of ferrocene due to protonation in tetrafluoroboric acid has been challenged⁷. In that brief note no pK value or spectroscopic evidence is offered for such reaction. As far as we know, no further reports of ferrocene instability in oxygen-free solutions have been published. Even if a slow decomposition of Fc would take place it would not affect its redox electrochemistry on the time scale of the drop-life of the dropping mercury electrode (DME).

Other “reference ions”, such as tetraethylammonium cation⁸ and rubidium cation⁹ have been proposed. The relative merits of different reference ion assumptions can be argued, but never proven. Our preference for metallocene/metallocenium couple at DME is driven by its reversible redox electrochemistry at DME. Ferrocene and cobaltocenium are reversible couples with the standard potentials in water 0.40 V (Fc/Fc⁺) and -0.94 V (Cob/Cob⁺), respectively. Both couples have a well-developed polarographic waves at DME¹⁰.

$$E_{1/2} = E^0 + \frac{2.303RT}{F} \log \frac{C_{\text{Mec}^+}}{C_{\text{Mec}}} + \frac{2.303RT}{F} \log \frac{f_{\text{Mec}^+}}{f_{\text{Mec}}} + \frac{2.303RT}{2F} \log \frac{D_{\text{Mec}}}{D_{\text{Mec}^+}}. \quad (6)$$

The calculated values of the standard potential of the metallocene/metallocenium couple (i.e. Fc/Fc^+ as well as Cob/Cob^+) vary by as much as 300 mV in a range of organic solvents, including e.g. DMSO and methanol^{6,11}. Unfortunately, the experimental verification of calculated values is burdened by a major uncertainty stemming from the use of aqueous (Ag/AgCl , KCl) reference electrode in organic solvents and its problematic liquid-junction potential¹². Realization of reference potential for electrochemical determination of acidity function is further complicated by the fact that the variation of hydronium ion activity is achieved by a variable ratio of the aqueous and organic components of the medium. In summary, liquid junctions cannot be used under those conditions and must be eliminated. The use of a stationary amalgam electrode as a reference has been suggested. It suffers from the similar problems as encountered by Strehlow, namely the surface contamination and low solubility of the neutral metallocene¹².

The use of DME as a “reference” electrode has been proposed by J. Heyrovský in the late fifties¹³. That suggestion was based on the well-known properties of the DME, namely its renewable and highly reproducible, atomically smooth surface. Unfortunately, a three-electrode potentiostat with high impedance input for the reference electrode was not available for its realization at that time.

The experimental realization of a liquid junction-free measurement is relatively simple. It hinges on the assumed invariability of the standard redox potential of the metallocene. In a normal three-electrode potentiostatic measurement the roles of the working and of the reference electrodes are reversed. Thus, the very-high-resistance glass electrode, which responds reversibly to the change of hydrogen ion activity, is connected to the high input impedance of the reference electrode terminal and the corresponding metallocene wave is recorded at the DME, which is connected as the working electrode. The “virtual” shift of the potential at which the polarographic wave is observed thus represents the variation of the potential of the glass electrode, while the redox potential of the metallocene reference electrode remains unchanged and serves as the reference¹⁴. The thus established acidity function H_{GM} is then given by the equation

$$-H_{\text{GM}} = \log a_{\text{H}^+} + \log f_{\text{Mec}}/f_{\text{Mec}^+} - \log \left(\frac{D_{\text{Mec}}}{D_{\text{Mec}^+}} \right)^{1/2}. \quad (7)$$

The major difference between Eqs (6) and (7) is the absence of the liquid-junction potential in the measurement. The correction due to differences in the ratio of diffusion coefficients is obviously negligibly small in most cases.

Because metallocenes are only sparsely soluble ($\sim 10^{-5}$ mol/l) in water at 25 °C, a rather high charging current is observed in the normal mode polarography during the standardization step (Fig. 1). That problem can be eliminated if pulse or differential pulse polarography is used. Acidity functions in several “non-ideal” media have been determined in this manner for the high activity of hydronium ion using Fc/Fc⁺ reference^{14,15} (Fig. 2a) and for strongly basic solutions using Cob/Cob⁺ reference^{16–18} (Fig. 2b). As the electrochemically determined acidity function is based on combination of glass indicator and metallocene redox couple reference electrode, it has been named H_{GF} for glass–ferrocene and H_{GC} for glass–cobaltocene, respectively. In solutions of high activity of alkali metal ions the glass electrode has to be replaced by hydrogen electrode and the corresponding acidity function has symbol H_{HC} . The general applicability of electrochemically based acidity function is illustrated in Fig. 3 and summarized in Tables I–IV. The detail values of the H_{GF} , H_{GC} and H_{HC} can be found in the original papers^{14–18} referenced in the tables, where they are compared with the con-

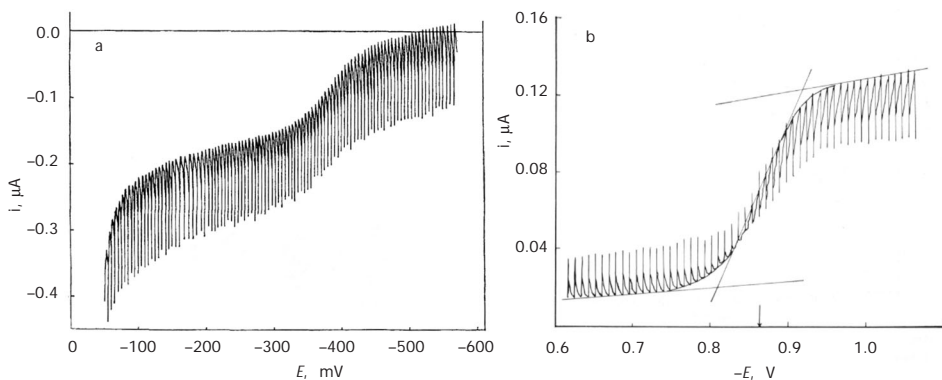


FIG. 1

DC polarograms of saturated solution of a ferrocene¹⁴ in 2.68 M HClO_4 b and 1×10^{-4} M cobalticinium acetate¹⁷ in 0.936 M aqueous ethylenediamine, measured at 25.0 °C under nitrogen. Forced drop time (2 s), SCE reference and Pt auxiliary electrodes

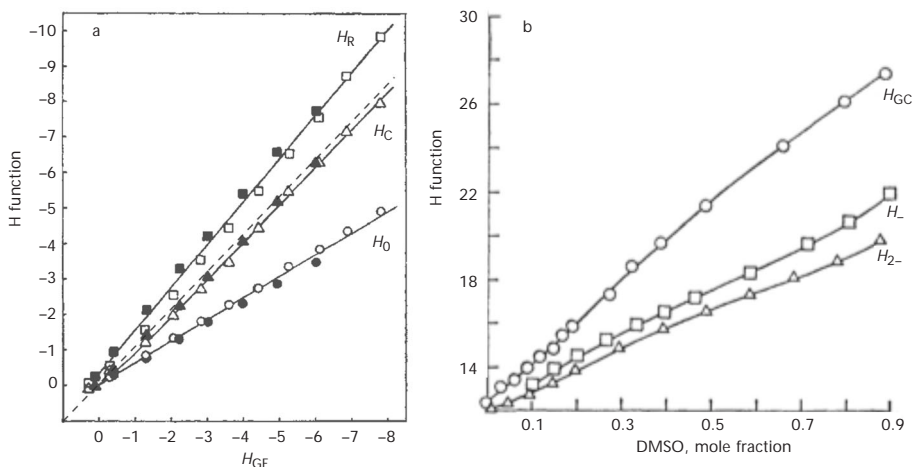


FIG. 2

a Comparison of three Hammett acidity functions (H_R , H_C and H_0) on the scale of H_{GF} ¹⁴. The dashed line indicates a perfect agreement between the conventional and potentiometric acidity function, showing a minimum solvation effect of the indicators based on carbon bases (H_C). b Comparison of two Hammett acidity functions, H_L and H_{2-} , with H_{GC} for the 0.01 M tetramethylammonium hydroxide–DMSO–water system. The concentration of the base is constant, the variable is mole fraction of DMSO^{17,19,20}

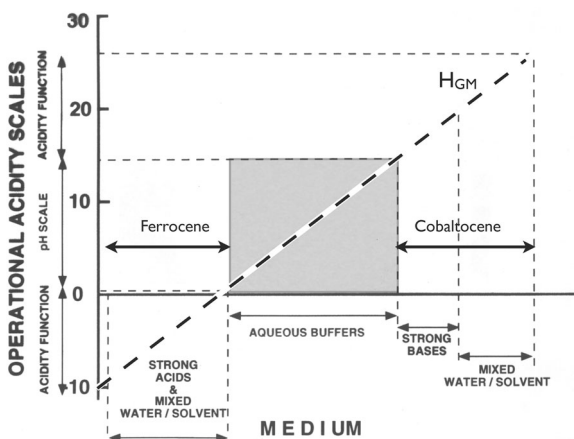


FIG. 3

Applicability of the acidity function H_{GM} , based on liquid junction-free potentiometric measurement of electrochemical cell comprising glass electrode and a dropping mercury electrode with ferrocene/ferricinium and cobaltocene/cobaltocinium redox couples

TABLE I
Values of H_{GF} function for acids at 25.0 °C

Reaction medium (concentration of acid)	H_{GF} range
H ₂ SO ₄ (0.25–11.0):H ₂ O	+0.64 to –8.75 ^a
HClO ₄ (0.25–7.5):H ₂ O	+0.55 to –6.70 ^a
H ₂ SO ₄ (0.25–10.0):20% EtOH; H ₂ O	+0.25 to –8.40 ^a
H ₂ SO ₄ (0.25–8.5):40% dioxane; H ₂ O	+2.15 to –6.78 ^a
H ₂ SO ₄ (0.25–5.5):60% dioxane; H ₂ O	+3.33 to –3.85 ^a
H ₂ SO ₄ (0.25–4.5):75% acetonitrile; H ₂ O	+2.78 to –6.38 ^a
H ₃ PO ₄ (1.00–11.0):H ₂ O	+0.33 to –5.66 ^b
H ₃ PO ₃ (0.50–11.0):H ₂ O	+0.72 to –3.18 ^b
CH ₃ SO ₃ H (0.50–10.0):H ₂ O	+0.07 to –5.78 ^b
PTS (0.50–4.5)	+0.18 to –4.16 ^b

^a From ref.¹⁴; polarograms were recorded in de-aerated solutions under nitrogen. Corning triple purpose “yellow glass” (low alkaline error) glass electrode Model 476022 was used in all experiments. ^b From ref.¹⁵ PTS, *p*-toluenesulfonic acid.

TABLE II
Values of H_{GC} function¹⁶ for aqueous bases at 25.0 °C

Reaction medium (concentration of base)	H_{GC} range
TMAH (0.1–2.8) ^a	12.75–16.65
TEAH (0.1–1.2) ^a	13.60–15.83
TBAH (0.1–1.4) ^a	13.25–17.80
BTMAH (0.5–2.6) ^a	13.68–17.95
Hydrazine (0.1–0.5) ^b	13.05–17.90
Ethylenediamine (0.1–1.0) ^b	14.45–22.00

Concentration given as ^a molar, ^b mole fraction.

TMAH, tetramethylammonium hydroxide; TEAH, tetraethylammonium hydroxide; TBAH, tetra(*n*-butyl)ammonium hydroxide; BTMAH, benzyltrimethylammonium hydroxide.

TABLE III
Values of H_{GC} function^{17,19,20} for aqueous–organic solvent mixtures

Reaction medium (mole fraction of organic solvent)	H_{GC} range
0.011 M TMAH in H ₂ O:DMSO (0.00–0.90)	12.30–27.65
0.047 M TMAH in H ₂ O:DMSO (0.00–0.65)	12.80–25.75
0.011 M TEAH in H ₂ O:DMSO (0.00–0.70)	12.30–23.75
0.011 M TMAH in H ₂ O:DMSO (0.00–0.55)	12.30–21.65
0.011 M TMAH in H ₂ O:DMSO (0.00–0.50)	12.30–21.25

TABLE IV
Values of acidity functions for solutions containing alkali metal cations¹⁸

Reaction medium (concentration)	H_{HC} range	H_{GC} range
KOH (0.25–7.50) ^a	13.45–18.09	–
NaOH (0.25–6.50) ^a	13.68–16.85	–
0.01 M NaOMe in MeOH:DMSO (0.0–0.99) ^b	16.80–25.63	16.89–22.82
0.011 M TMAH in H ₂ O:TMS (0.0–0.75) ^b	12.68–21.54	12.74–21.66

Concentrations given as ^a molar, ^b mole fraction.

ventional Hammett functions. Obviously, the electrochemical approach can be used for determination of activities of other ions under extreme conditions, when the use of a liquid-junction reference electrode would not be possible.

CONCLUSIONS

The use of metallocene reference electrode (potential), realized at dropping mercury electrode demonstrates a solution to the persistent problem, namely the need for defined and stable reference potential in potentiometry in non-ideal media. In the determination of the activities of ionic species under extreme conditions, the extra-thermodynamic assumption of the constant ratio of solvation energies of the metallocene/metallocenium redox couple allows experimental elimination of the troublesome liquid-

junction potential. Such approach is arguably the best approach for realization of reference potential under extreme conditions in solution. With the acceptance of that caveat, the use of aqueous standard state (i.e. standard buffers) over extremely broad range of activities is possible.

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