

## PROBLEMS OF ELECTROCHEMICAL CONTROLS OF OXIDATION-REDUCTION SYSTEMS IN AQUEOUS-ORGANIC AND NONAQUEOUS MEDIA. THE rH INDEX WITH ESTABLISHMENT OF THE RELEVANT SCALES AND STANDARDS

Luigi FALCIOLA<sup>1</sup>, Patrizia R. MUSSINI<sup>2</sup> and Torquato MUSSINI<sup>3,\*</sup>

*Department of Physical Chemistry and Electrochemistry, University of Milano, Via Venezian 21, 20133 Milano, Italy; e-mail: <sup>1</sup> luigi.falciola@unimi.it, <sup>2</sup> patrizia.mussini@unimi.it,*

*<sup>3</sup> torquato.mussini@unimi.it*

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*Dedicated to the colleague Professor Sergio Roffia on the occasion of his retirement, for his outstanding contributions in various areas of electrochemistry.*

The state and problems of the electrochemical controls of oxidation-reduction systems in aqueous-organic and nonaqueous solvent media with particular emphasis on the rH index of the reducing power of such systems are discussed. In the frame of a generalized treatment of the rH-metric domain, the key definitions, the acquisition of primary rH<sub>s</sub> standards, the comparison of rH scales in different solvent media, and the recommended procedure of rH<sub>x</sub> determination are described. The most recent results here obtained in the studies of the behaviour of the quinhydrone electrode with respect to the hydrogen gas electrode, and of the key cell Pt|H<sub>2</sub>|H<sub>2</sub>O|HgO|Hg|Pt are reported, and the guidelines for further development are outlined.

**Keywords:** rH scales; rH standards; Quinhydrone electrode; Hydrogen gas electrode; Redox processes; Solvent effects; Binary mixtures.

It is regrettable to realize that, as far as the acid-base and the oxidation-reduction equilibria in aqueous, nonaqueous and mixed solvents are concerned, the level and extension of treatments in the relevant literature are deeply unequal, in spite of the current great theoretical and application interest. In fact, on one hand, especially since 1970, the acid-base equilibria and related controls have found a rather exhaustive assessment in Bates's admirable book<sup>1</sup>, in a number of scientific articles and monographs<sup>1,2</sup>, and in various IUPAC recommendation documents<sup>3-7</sup>. On the other hand, the oxidation-reduction equilibria and related controls have hitherto received

scarce attention<sup>8-10</sup>, especially by the standardizing organizations, and thus some systematization is overdue.

Aim of this paper is to present a unified scheme for the definitions and procedures of control of oxidation-reduction systems in any type of solvent medium (aqueous, aqueous-organic, and nonaqueous): particular attention is given to the description of the relevant scale ranges and primary standards required to perform measurements of the rH index<sup>11,12</sup> in the above media.

In general terms (*i.e.* for any type of solvent), the notional definition of rH, which is an index of the reducing power of the redox system considered, is

$$\text{rH} = -\log (p_{\text{H}_2}) , \quad (1)$$

where  $p_{\text{H}_2}$  would be that hydrogen gas pressure at which the potential of the hydrogen electrode,

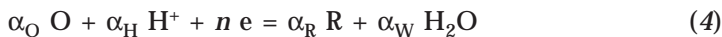
$$E_{\text{H}^+|\text{H}_2} = E_{\text{H}^+|\text{H}_2}^\circ - k \text{pH} + (k/2) \text{rH} , \quad (2)$$

in the same medium as the redox system studied, would be identical to the redox potential  $E_{\text{O|R}}$  of the latter; here  $k = (\ln 10)RT/F$ . As such, the rH index together with the pH index and the redox potential  $E_{\text{O|R}}$  constitutes an interrelated triade, which has been recently illustrated<sup>8,9</sup> and rationalized in terms of Pourbaix's  $E_{\text{O|R}}$  potential/pH diagrams in pure water solvent. The difficulties in rH measurements in mixed aqueous-organic solvents and the limits of their rH scales comparability will be dealt with in the present paper.

Equalling  $E_{\text{H}^+|\text{H}_2}$ , as given by Eq. (2), to the expression for the redox potential  $E_{\text{O|R}}$

$$\begin{aligned} E_{\text{O|R}} = E_{\text{O|R}}^\circ + (k/n)\{\alpha_{\text{O}} \log (a_{\text{O}}) - \alpha_{\text{R}} \log (a_{\text{R}}) - \alpha_{\text{W}} \log (a_{\text{W}})\} - \\ - \alpha_{\text{H}}(k/n) \text{pH} \end{aligned} \quad (3)$$

related to the general redox reaction

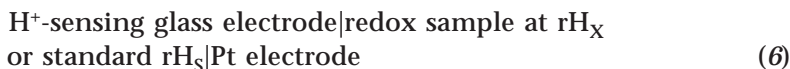


we have

$$\begin{aligned} \text{rH} = & (2/k)E_{\text{O|R}} - (2/k)E_{\text{H}^+|\text{H}_2}^\circ + 2 \text{pH} = (2/k)[E_{\text{O|R}}^\circ - E_{\text{H}^+|\text{H}_2}^\circ] + \\ & + (2/n)\{\alpha_{\text{O}} \log(a_{\text{O}}) - \alpha_{\text{R}} \log(a_{\text{R}}) - \alpha_{\text{W}} \log(a_{\text{W}})\} + 2(1 - \alpha_{\text{H}}/n) \text{pH}, \quad (5) \end{aligned}$$

where  $E^\circ$  denotes the standard potentials of the electrodes marked by subscripts;  $a_{\text{O}}$ ,  $a_{\text{R}}$ , and  $a_{\text{W}}$  are the activities of the oxidized species O, of the reduced species R, and of the water W, respectively, and the  $\alpha$ 's are the corresponding stoichiometric coefficients;  $n$  is the number of electrons involved in the redox reaction. Many redox couples, inorganic or organic, have  $\alpha_{\text{H}} = 0$  (i.e. pH-independent  $E_{\text{O|R}}$ ) which also implies  $\alpha_{\text{W}} = 0$ .

Equation (5) is the fundamental expression for  $\text{rH}_X$  determination of any redox system and would, as such, require measuring a lot of independent quantities (with related calibrations). The most convenient procedure of  $\text{rH}_X$  measurement is, however, of comparative type<sup>9,10</sup>, based on measuring the potential differences  $E_X$  (on the sample of unknown  $\text{rH}_X$ ) and  $E_S$  (on the known  $\text{rH}_S$  standard) of the cell



for which the functional expression is

$$\text{rH}_X = \text{rH}_S + (2/k)(E_X - E_S) \quad (7)$$

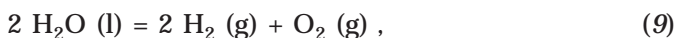
and requires the availability of reference standards  $\text{rH}_S$  appropriate to the normal  $\text{rH}$  range in the solvent medium considered. These  $\text{rH}$ -metric standards are dealt with in Results and Discussion. It is worthwhile to underline that the cell (6) and Eq. (7) do not include liquid junction potentials, in contrast to the parallel functional expression for pH measurements.

It has been exhaustively explained that, for an adequate treatment of the  $\text{rH}$  scale, it is necessary to consider also the complementary  $\text{rO}$  index of the oxidizing power<sup>8-10</sup> of the same redox system under control, i.e.

$$\text{rO} = -\log(p_{\text{O}_2}), \quad (8)$$

where  $p_{O_2}$  denotes that pressure of oxygen gas which would render the potential of the oxygen electrode equal to the redox potential  $E_{O|R}$  of the system considered.

The rH scale width (together with the rO one) is conventionally related to the value at 298.15 K of the equilibrium constant  $K_{WG}$  pertaining to the equilibrium of gaseous dissociation of liquid water:



whose expression is

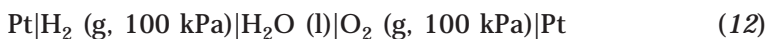
$$K_{WG} = p_{\text{H}_2}^2 p_{\text{O}_2} / (x_{\text{W}} f_{\text{W}})^2, \quad (10)$$

where  $a_{\text{W}} = x_{\text{W}} f_{\text{W}}$  = activity of liquid water, and  $x_{\text{W}}$  and  $f_{\text{W}}$  are the corresponding mole fractions and related activity coefficients, respectively.

The  $K_{WG}$  constant is strictly linked with the following thermodynamic equation:

$$2.303RT \text{p}K_{WG} = \Delta G^\circ = 4FE^\circ_{12} = -2\mu^\circ_{\text{W}} \quad (11)$$

where  $\text{p}K_{WG} = -\log(K_{WG})$ ,  $\Delta G^\circ$  is the standard Gibbs energy change for the reaction (9),  $\mu^\circ_{\text{W}}$  is the standard chemical potential of the liquid water (henceforth in subscripts and superscripts the water  $\text{H}_2\text{O}$  will be denoted W), and  $E^\circ_{12}$  is the standard potential difference of Grove's-type cell (12) assumed to behave reversibly in the following limiting configuration.



In fact, the overall reaction of cell (12), whose pd  $E_{12}$  expression is

$$E_{12} = E^\circ_{12} - (k/2) \log(x_{\text{W}} f_{\text{W}}) \quad (12a)$$

is exactly the opposite to reaction (9). Measuring  $E_{12}$  faces the following problems: (i) the notorious difficulty of setting up a rigorously reversible oxygen gas electrode, and (ii) the necessity of adding small hydroxide con-

centrations  $m_{\text{KOH}}$  to water  $W$  or to the aqueous-organic solvent  $Z = W + S$  ( $S = \text{nonaqueous co-solvent}$ ) to ensure electric conductance of the cell and stability of the oxygen electrode. The former difficulty is circumvented by using the alternative, easy-to-handle, and equivalent cell (16) described in Results and Discussion; the latter condition obviously introduces ionic interactions and causes alterations to the water mole fraction  $x_W$ , which makes it mandatory to extrapolate the measured  $E_{12}$  to zero ionic strength to obtain the limiting value  $E^*_{12}$ . The functional equation (12a) thus becomes

$$E^*_{12} = E^{\circ}_{12} - (k/2) \log (x_W f_W) . \quad (13)$$

From Eqs (1), (8), (9) and (10) one gets

$$\text{p}K_{\text{WG}} = 2 \text{rH} + \text{rO} + 2 \log (x_W f_W) . \quad (14)$$

Eliminating  $\log (x_W f_W)$  from Eqs (13) and (14) and remembering Eq. (11), one gets for each  $x_W$  studied

$$4E^*_{12}/k = 2 \text{rH} + \text{rO} . \quad (15)$$

The ranges of both the normal rH scale and the normal rO scale for the general solvent  $Z = W + S$  are fixed by Eq. (15). These ranges are different and unsymmetrical, and the redox neutrality points<sup>13</sup> differ from each other and from the midscale points. As summarized in Table I, in terms of rH scale, the lower end of the range (*i.e.* the “zero” of rH scale) is  $\text{rH}_{\text{min}} = 0$  (conventional point of maximum reducing power, corresponding to the standard state pressure of  $p_{\text{H}_2} = 100 \text{ kPa}$ ). The upper end (implying  $\text{rO} = 0$ ) is  $\text{rH}_{\text{max}} = 2E^*_{12}/k$  (minimum reducing power). For the complementary “normal rO range” there corresponds the upper end  $\text{rO}_{\text{max}} = 4E^*_{12}/k$  (conventional point of minimum oxidizing power, implying  $\text{rH} = 0$ ), whereas the lower end (zero of rO scale) is  $\text{rO}_{\text{min}} = 0$  (maximum oxidizing power, corresponding to the standard state pressure of  $p_{\text{O}_2} = 100 \text{ kPa}$ ). In the particular case of water, where  $E^*_{12} \equiv E^{\circ}_{12} = 1.2291 \text{ V}$  at 298.15 K, we have the following ranges:  $0 < \text{rH} < 41.55$  and  $0 < \text{rO} < 83.10$ , respectively<sup>8-10</sup>; furthermore,  $\text{rH}_{\text{neutr}} = 27.60$  ( $\neq \text{rH}_{\text{mid}} = 20.77$ ), and  $\text{rO}_{\text{neutr}} = 27.90$  ( $\neq \text{rO}_{\text{mid}} =$

41.55). On Pourbaix's potential vs pH diagrams<sup>14</sup>, the  $rH = 0$  and  $rO = 0$  values mark the limits of the thermodynamic stability band of water<sup>8</sup>.

At the redox neutrality point<sup>8-14</sup>, which implies  $p_{H_2} = 2p_{O_2}$  and  $rH_{\text{neutr}} = rO_{\text{neutr}} - \log 2$  (refs<sup>8-14</sup>), we have  $rH_{\text{neutr}} = (4E^*_{12}/k - \log 2)/3$ , and  $rO_{\text{neutr}} = 4E^*_{12}/k - 2 rH_{\text{neutr}} = (4E^*_{12}/k + 2 \log 2)/3$ .

## EXPERIMENTAL

The design of the hydrogen electrodes was described in our works on pH standardization in aqueous-organic solvent mixtures<sup>15</sup>. The quinhydrone electrodes were prepared as in our recent investigations on  $rH$  standardization in water<sup>10</sup>. The mercury oxide electrodes for cell (16) were prepared as in our earlier study on oxide electrodes<sup>16</sup>. The cell potential differences were measured at  $298.15 \pm 0.10$  K with a high-input-impedance model 619 Keithley differential electrometer and were accurate to within  $\pm 0.05$  mV. The thermostatic apparatus was the same as described earlier<sup>17</sup>. All solutions were prepared by weight from redistilled deionized water, reagent-grade chemicals and organic solvents.

TABLE I

Some correlations of quantities  $rH$  and  $rO$  with related standards as functions of  $E^*_{12}$  of cell (12) at 298.15 K in terms of Eqs (14) and (15)

Quantity	$rH$	$rO$
Minimum value (lower scale end)	0 (maximum reducing power)	0 (maximum oxidizing power)
Maximum value (upper scale end)	$2E^*_{12}/k$ (minimum reducing power)	$4E^*_{12}/k$ (minimum oxidizing power)
Midscale point	$E^*_{12}/k$	$2E^*_{12}/k$
Redox neutrality point <sup>11</sup>	$(4E^*_{12}/k - \log 2)/3$	$(4E^*_{12}/k + \log 2)/3$
Quinhydrone-based $rH_S$ standard in W	23.66	35.78
Quinhydrone-based $rH_S$ standard in Z <sup>a</sup>	23.66 <sup>a</sup>	$4E^*_{12}/k - 2 \times 23.66^a$
Hydro-quinhydrone-based $rH_S$ standard in W	20.73	41.64
Hydro-quinhydrone-based $rH_S$ standard in Z <sup>a</sup>	20.73 <sup>a</sup>	$4E^*_{12}/k - 2 \times 20.73^a$
Quino-quinhydrone-based $rH_S$ standard in W	25.34	32.42
Quino-quinhydrone-based $rH_S$ standard in Z <sup>a</sup>	25.34 <sup>a</sup>	$4E^*_{12}/k - 2 \times 25.34^a$

<sup>a</sup> Proposable  $rH_S$  standards calculated assuming exact invariancy of the standard potential difference of cell (21) with varying the solvent Z.

## RESULTS AND DISCUSSION

*Normal Ranges of rH Scales*

For the reasons explained above, the cell (12) has been here advantageously and accurately replaced by a reversible mercury-oxide-based cell of the following configuration:



whose potential difference  $E_{16}$  can be readily shown to be related to  $E_{12}$  by the equation

$$E_{12} = E_{16} - \mu^\circ_{\text{HgO}}/2F. \quad (17)$$

From international tabulations of standard thermodynamic functions<sup>18</sup> we find the accurate value  $\mu^\circ_{\text{HgO}} = -58555 \text{ J mol}^{-1}$  (of course, independent of the composition of the aqueous-organic solvent Z), and, consequently, we obtain  $-\mu^\circ_{\text{HgO}}/2F = 0.30344 \text{ V}$ , using  $F = 96485.31 \text{ C mol}^{-1}$ . Thus,

$$E_{12} = E_{16} + 0.30344 \text{ V}, \quad \text{at } 298.15 \text{ K}. \quad (18)$$

Of course, also in the cell (16) the solutions must contain indispensable small concentrations of KOH. The effect of the interactions caused by the KOH presence has, therefore, been eliminated by extrapolation of  $E_{16}$  to infinite dilution ( $m_{\text{KOH}} = 0$ ) to obtain the limiting value  $E^*_{16}$  to be inserted in Eq. (18) giving

$$E^*_{12} = E^*_{16} + 0.30344 \text{ V}, \quad \text{at } 298.15 \text{ K}, \quad (19)$$

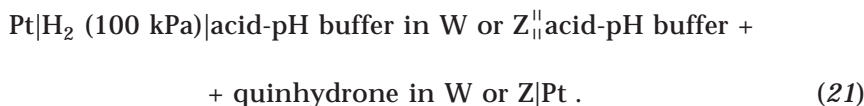
which is the operational equation used here. For instance, in the acetonitrile-water mixture at mass fraction of acetonitrile of 0.5, we find  $E^*_{12} = 1.2376 \text{ V}$ . Therefore the upper end of the conventional range of rH scale in this mixed solvent is  $\text{rH}_{\text{max}} = \text{rH}_{\text{range}} = 2E^*_{12}/k = 41.84$ , to be compared with the parallel value in pure water: 41.55. The difference is not dramatic but might be much greater in other solvent mixtures.

*Primary rH-Metric Standards in the General Solvent Z*

The quinhydrone redox system (*i.e.*, the equimolar 1,4-benzoquinone [Q]-hydroquinone [QH<sub>2</sub>] mixture), whose theory and behaviour were expounded in detail by Ives and Janz<sup>8</sup>, provides the key rH-metric standard rH<sub>S</sub>. The establishment of the latter is in terms of the following rationale, which follows the same tracks of Eq. (5). Equalling the potential of the quinhydrone electrode,  $E_{\text{quinhy}} = E^{\circ}_{\text{quinhy}} + k \log(a_{\text{H}^+}) = E^{\circ}_{\text{quinhy}} - k \text{pH}$ , with that of the hydrogen electrode,  $E_{\text{H}^+|\text{H}_2} = E^{\circ}_{\text{H}^+|\text{H}_2} + k \log(a_{\text{H}^+}) - k \log(p_{\text{H}_2}) = E^{\circ}_{\text{H}^+|\text{H}_2} - k \text{pH} + (k/2) \text{rH}$ , it turns out that conceptually irrespective of the solvent considered

$$\text{rH} = 2(E^{\circ}_{\text{quinhy}} - E^{\circ}_{\text{H}^+|\text{H}_2})/k = 2E^{\circ}_{21}/k = \text{rH}_S, \quad (20)$$

where  $E^{\circ}_{21}$  is the standard potential difference of cell (21):



In this cell there is the same low H<sup>+</sup> concentration on both sides of the junction ||, and there is no appreciable liquid junction potential. Equation (20) constitutes an important asset to the electroanalyst in that it is used for establishing primary rH-metric standards based on low-acidity saturated quinhydrone solutions. In water,  $E^{\circ}_{21} = 0.69975 \text{ V}$  at 298.15 K, therefore  $\text{rH}_S(\text{quinhy}, \text{W}) = 23.66$  at 298.15 K, as quoted in Tables I ad II. For convenience, Table II also quotes the parallel standard redox potentials useful for the calibration of redox electrodes and the corresponding reference pH values. The rH<sub>S</sub> values are temperature-dependent like the parent values  $E^{\circ}_{21}$ . Since accurate values of the latter quantity in the solvent water are available<sup>8</sup>, then rH<sub>S</sub> values at temperatures other than 298.15 K can be readily obtained. As shown by Eq. (15), the rO value complementary to rH in water is:  $\text{rO}(\text{quinhy}, \text{W}) = 4E^{\circ}_{12}/k - 2 \text{rH}(\text{quinhy}, \text{W}) = 35.78$  (see Table I).

Let us now turn to considering the aqueous-organic solvent mixtures Z. First of all, both the potential of the hydrogen gas electrode and that of the quinhydrone electrode are subject to the primary medium effect<sup>20</sup> on the solvated H<sup>+</sup> ion, upon transferring them from water W to the aqueous-



organic solvent Z, which, in thermodynamic terms, causes the well-known problems of non-comparability of pH scales in different solvents. However, the overall reaction of the key cell (21) is  $\text{H}_2$  (g, 100 kPa) + Q = QH<sub>2</sub>; hence, it is not only independent of the acid concentration but also of the composition of the aqueous-organic solvent mixture Z. Thus, provided that the quinhydrone-saturated solution is not alkaline and does not contain aliquots of amino or ammonium compounds or strong oxidants or proteins<sup>8</sup>, one should reasonably expect that the potential difference  $E_{21}$  of cell (21), which therefore coincides with its standard potential difference  $E_{21}^\circ = E_{\text{quinhy}}^\circ - E_{\text{H}^+|\text{H}_2}^\circ$ , will be independent of the Z composition or, in other words, there is no primary medium effect. Thus Eq. (20) is valid and applicable to any such Z-compatible quinhydrone system, and the quinhydrone-based rH<sub>S</sub> standard is likely to be invariant with varying composition of the aqueous-organic solvent Z (irrespective of the fact that the normal rH range might change with Z composition) and acts as a large intersolvent rH-metric standard, its value being rH<sub>S</sub> (quinhy,Z) = 23.66 at 298.15 K, exactly as in W.

The potential difference  $E_{21}$  of the cell (21) at 298.15 K has been measured systematically, six times, in aqueous-organic solvent mixtures Z = W + S, where the co-solvents S investigated were acetonitrile, methanol, 1,4-dioxane, glycerol, and formamide, over a wide range of mass fractions  $w_S$ . The  $E_{21}$  values, together with the corresponding rH<sub>S</sub> values, are given in Table III.

TABLE II

Some reference solutions proposed as rH-metric standards rH<sub>S</sub> at 298.15 K and for the calibration of the redox electrode at  $E_{\text{O|R}}$  in water medium<sup>10</sup>

Standard redox solutions in water	pH	$E_{\text{O R}}, \text{V}$	rH
0.05 m potassium tetraoxalate buffer solution, saturated with quinhydrone	1.65	0.6021	23.66
0.01 M HCl + 0.09 M KCl solution (Veibel's solution <sup>1,19</sup> ), saturated with quinhydrone	2.08	0.5767	23.66
0.05 m potassium hydrogen phthalate buffer solution, saturated with quinhydrone	4.01	0.4625	23.66
0.01442 M Na <sub>2</sub> HPO <sub>4</sub> + 0.02644 M NaH <sub>2</sub> HPO <sub>4</sub> buffer solution, saturated with quinhydrone	7.00	0.2856	23.66

TABLE III  
 Measured potential differences  $E_{21}$  of the quinhydrone-electrode cell (21) with corresponding rH values in W-S aqueous-organic solvent mixtures with mass fraction  $w_S$  of the organic co-solvent S. Temperature 298.15 K

$w_S$	Methanol			Acetonitrile			1,4-Dioxane			Glycerol		
	$E_{21}, V$	rH	$w_S$	$E_{21}, V$	rH	$w_S$	$E_{21}, V$	rH	$w_S$	$E_{21}, V$	rH	$w_S$
0.000	0.69976	23.66	0.000	0.69976	23.66	0.000	0.69976	23.66	0.000	0.69976	23.66	0.000
0.500	0.71295	24.10	0.500	0.70011	23.67	0.500	0.71667	24.23	0.500	0.71388	24.13	0.500
0.500	0.71130	24.05										
0.500	0.71253	24.09										
0.500	0.71327	24.11										
0.500	0.71115	24.04										
0.500	0.71253	24.09										
0.700	0.71691	24.24	0.700	0.70483	23.83	0.700	0.72082	24.37	0.700	0.71163	24.06	0.700
0.700	0.71498	24.17	0.700	0.70765	23.92	0.700	0.72250	24.43	0.700	0.70916	23.97	0.700
0.700	0.71650	24.22	0.700	0.70374	23.79	0.700	0.72100	24.37	0.700			0.700
0.700	0.71638	24.22	0.700	0.70395	23.80	0.700	0.71841	24.29	0.700			0.700
0.700	0.71423	24.15				0.700	0.72250	24.43	0.700			0.700
0.700	0.71588	24.20				0.700	0.72250	24.43	0.700			0.700
						0.875	0.71823	24.28	0.875			0.875
						0.875	0.71218	24.08	0.875			0.875
						0.875	0.71408	24.14	0.875			0.875
						0.875	0.71860	24.29	0.875			0.875
						0.875	0.71170	24.06	0.875			0.875
						0.875	0.71310	24.11	0.875			0.875

TABLE III  
(Continued)

Methanol			Acetonitrile			1,4-Dioxane			Glycerol		
$w_S$	$E_{21}, V$	rH	$w_S$	$E_{21}, V$	rH	$w_S$	$E_{21}, V$	rH	$w_S$	$E_{21}, V$	rH
0.900	0.71838	24.29	0.900	0.69786	23.59						
0.900	0.71785	24.27	0.900	0.70095	23.70						
0.900	0.71943	24.32	0.900	0.70112	23.70						
0.900	0.71855	24.29	0.900	0.69993	23.66						
0.900	0.71783	24.27									
0.900	0.71900	24.31				0.946	0.71123	24.04			
						0.946	0.71408	24.14			
						0.946	0.71643	24.22			
						0.946	0.71011	24.01			
						0.946	0.71418	24.14			
						0.946	0.71535	24.18			
0.950	0.71881	24.30	0.950	0.69480	23.49						
0.950	0.71520	24.18	0.950	0.69298	23.43						
0.950	0.71770	24.26	0.950	0.69589	23.53						
0.950	0.71709	24.24									
0.950	0.71493	24.17									
0.950	0.71697	24.24									
			0.000	0.6132	20.73 <sup>a</sup>						
			1.000	0.6155	20.81 <sup>a</sup>						
									1.000	0.71768	24.45
										Formamide	

<sup>a</sup> The hydro-quinhydrone electrode replaces the quinhydrone electrode in cell (21).

It is evident that the expected invariability of  $E_{21}$  and  $rH_S$  with varying  $w_S$  is fulfilled rather satisfactorily, especially with such co-solvents as acetonitrile, the general average result being  $24.10 \pm 0.25$  in  $rH_S$ . (Incidentally, exact invariability for the quinhydrone-based  $rH_S$  standard was tacitly assumed for the exemplifications in Table I.) The small deviations observed with respect to the figures in pure water solvent may well be due to some of the several reasons classified in the fundamental review by Ives and Janz<sup>8</sup>, e.g., small alterations of the exact Q-QH<sub>2</sub> equimolarity and of the unit ratio of activity coefficient  $f_Q / f_{QH_2}$ , chemical reactivity of the co-solvent with Q and/or QH<sub>2</sub>, acid error, and so on.

To attain even more stringent results, it is desirable to perform an extension of measurements of the potential of the cell (21) replacing the quinhydrone electrode with its variants known as "quino-quinhydrone" or "hydro-quinhydrone". This would likely ensure complete freedom from solvent composition and acid/salt errors<sup>8</sup>, so that both  $E_{21}$  (which coincides with the relevant standard potential  $E_{21}^\circ$ ) and  $rH_S$  would be invariant on passing from W to Z. The expected invariant standard potentials  $E_{21}^\circ$  would be 0.7496 and 0.6132 V at 298.15 K (ref.<sup>8</sup>), which correspond to  $rH_S$  values of 25.34 and 20.73, respectively. This alternative has here been explored with the hydro-quinhydrone system in acetonitrile at 298.15 K, giving  $E_{21}^\circ = 0.6155$  V and  $rH = 20.81$  against  $E_{21}^\circ = 0.6132$  V and  $rH = 20.73$  in water, respectively, which closely satisfies the expectations (cf. Table III, bottom of 2nd column).

### *Possible Extension of the rH-Index Methodology to Pure Nonaqueous Media*

Extension of the  $rH$  methodology to pure nonaqueous media  $S$  essentially faces three problems: (i) how to define  $rH$  scale ranges in such media; (ii) how to determine appropriate  $rH_S$  standards; and (iii) to assess a methodology for  $rH_X$  measurement. The problems (ii) and (iii) do not cause remarkable difficulties, as shown later on, but the problem (i) implies definitional focussing and requires inspection of the applicability of the cells and equations mentioned above to the aqueous-organic mixed media. For discussion, the following points should be reminded.

1. The hydrogen gas electrode behaves reversibly in practically all solvents<sup>21</sup> and, as such, constitutes the pivot for any possible  $rH$ -metric extension to pure nonaqueous solvents.

2. The quinhydrone electrode can function reversibly in a number of nonaqueous solvents  $S$  (obviously excluding ammonia and amines, but not amides and nitriles) and keeps practically invariant its standard electrode

potential referred to that of the hydrogen electrode in the same solvent (0.69976 V at 298.15 K, to which corresponds  $rH_S = 23.66$ ), as verified *e.g.* in acetonitrile and other solvents, if we make the short extrapolation to  $w_S = 1$  for the figures in Table III.

3. Therefore, any acid (buffered) solution saturated with quinhydrone in the above selected solvents S does practically offer an intersolvent rH standard at hand.

4. It is quite possible, even if not so easy, to construct Pourbaix's  $E_{O/R}$  vs pH diagrams (once known the pertinent pH scale ranges and appropriate pH-metric standards in the relevant solvent S) and to draw iso-rH curves, as shown in refs<sup>8-11</sup>.

5. The basic definition  $rH = -\log p_{H_2}$  can well function in pure non-aqueous solvents S because also in S there can exist redox systems (of electrode potential  $E_{O/R}$  measured against the hydrogen electrode in S) of which a measure of the reducing power is desirable.

6. The lower scale end with  $rH = 0$  (nominal maximum reducing power) can exist also in S; obviously all values of  $rH > 0$  indicate lower reducing powers than at  $rH = 0$  for the redox system considered, just as in water and in any mixed solvent  $Z = W + S$ .

7. The  $rH_X$  measurement in S can be performed by the same cell (6) recommended for  $rH_X$  measurements in W or in the solvent mixtures  $Z = W + S$ , provided that in pure S the  $H^+$ -sensing glass electrode works properly, since at least one  $rH_S$  standard for S exists (see points 2. and 3.), as required by the functional equation (7); as a matter of fact, the glass electrode was found to work properly in many nonaqueous solvents<sup>22,23</sup>.

8. As remarked above discussing the case of mixtures  $Z = W + S$ , also with S there is no primary medium effect on rH, since there is no involvement of the ionic species  $H^+$  but the uncharged species  $H_2$ .

The chief difficulty is of definitional nature. In fact, the equilibrium (9) of gaseous dissociation of liquid water through its constant  $K_{WG}$  (Eqs (10) and (11)) defines the scale range of rH (combined with that of rO) for the solvent water and for the unlimited number of the possible aqueous-organic solvent mixtures W-S, where water is always one component of the binary solvent except the obvious limiting case of pure S. Now it requires some effort of imagination to think of an oxygen gas electrode (linked to the rO definition in Eq. (8)) or a mercury oxide electrode (cell diagram (16) and scale ranges defined by Eq. (15)) as working in pure S without presence of some water. Good help comes from consideration of the observed general trend of rH scale ranges upon varying the composition of the mixtures W-S. For instance, in preliminary determinations at 298.15 K, we obtained

the following results: (i) in acetonitrile at  $w_S = 0.5$ ,  $E^*_{12} = 1.2376$  V,  $rH_{\max} = 41.84$ ; (ii) in *N*-methylformamide at  $w_S = 0.99$ ,  $E^*_{12} = 1.2690$  V,  $rH_{\max} = 42.92$ . It is apparent that, upon approaching the unity mass fraction of S in the mixture, there is very little variation of  $E^*_{12}$  and the corresponding  $K_{WG}$ , account being taken of the experimental uncertainty limits. Therefore, extrapolation of this trend to zero mass fraction of water (or, better, to infinitesimally small water content or to "trace" water) would be legitimate and physically significant, and the limiting value at  $w_S = 1$  could be taken as representing the rated scale range of rH for each specific solvent S considered. It is worthwhile to remind that a similar conceptual approach is used in the thermodynamics of binary electrolyte mixtures MX + NY at constant total molality, where the activity coefficient of MX component can be determined in real terms upon decreasing the MX molality until getting the "trace" MX activity coefficient in the limit when MX is totally replaced by NY. The scheme proposed here would, until the standardization organizations will decide, allow application of the rH-metric methodology in a manner coherent for water, aqueous-organic mixtures, and pure non-aqueous media.

## CONCLUSIONS

From the foregoing results it may be concluded that:

1. The more sensible manner of controlling how a reduction or oxidation process comparatively proceeds in different solvents Z is to compare the current measured rH values with the pertinent-scale redox neutrality  $rH_{\text{neutr}}$  values: this is wholly analogous to what happens with any measured pH value, which is interpreted as compared with the acid-base neutrality  $pH_{\text{neutr}}$ .

2. The recommended routine procedure of rH measurements in the solvent Z is analogous to that currently applied in aqueous medium<sup>1</sup>, and is based on potential difference  $E_X$  and  $E_S$  combined measurements with cell (6) using of the pertinent operational equation (7).

3. To judge the stable functionality of the glass electrode in connection with point 2., it is worthwhile to outline that the potential difference of the cell Pt|H<sub>2</sub> (100 kPa)|HCl ( $m \ll$ ) in W or Z|glass electrode, measured at 298.15 K in water and in all the solvents Z considered here, was  $0.6135 \pm 0.0008$  V, where 0.0008 V corresponds to 0.02 in rH.

4. The widths of the rH scales in aqueous-organic solvent mixtures vary with solvent composition, but not as dramatically as the widths of pH scales. Extensive systematic work, with special attention to the highest

mass fractions of co-solvents, is urgently needed to fill the existing huge lack of data. In this context, the cell (16) provides the most suitable methodology.

5. Unlike the features of the acid-base equilibria domain, where the neutral pH point coincides with the midscale pH in each solvent Z, in the redox equilibria domain the neutral rH point does not coincide with the midscale rH point.

6. For the time being, at least as a first reasonable approximation, in the absence of exhaustive information on  $pK_{WG}$  in a nonaqueous solvent S, and awaiting emanation of *ad hoc* criteria from the standardization bodies, the range of rH-metric scale in water can be used for the rH-metry in S.

7. Unlike the pH-metric field, where no standard buffer solution has invariant  $pH_S$  value upon shifting from one to another solvent Z, in the redox field there are  $rH_S$  standards (*e.g.* those based on quinhydrone-saturated acid solutions) that remain practically unchanged, which is an important bonus to the electroanalysts.

8. Accurate and systematic investigations are still needed to extend the determination of new "central"  $rH_S$  standards based, *e.g.*, on the reversible quino-quinhydrone as well as the hydro-quinhydrone redox systems<sup>8</sup>, which would avoid the notorious "salt errors"<sup>8</sup>. However, the values of these additional  $rH_S$  standards are again situated close to the midscale point.

9. Contrary to what happens in pH-metric scales in Z, whose span is rather uniformly covered by  $pH_S$  standards, for the rH-metric scales in Z the availability of  $rH_S$  standards is meager and virtually limited to acid buffer solutions saturated with quinhydrone which provide  $rH_S$  values close to the midscale point (with the only exception of aqueous  $rH_S$  standards)<sup>10</sup>.

10. In connection with point 9., a sufficient number of  $rH_S$  standards close to the upper as well as to the lower end of rH scale are to be singled out and characterized operationally. For these the same experimental scheme applied recently to pure aqueous solution<sup>10</sup> for the  $rH_S$  standards based on the Cr(VI)/Cr(III) couple is appropriate.

11. In connection with point 2., it is necessary to outline that the applicability of cell (6) to rH measurements in nonaqueous S is associated with the functionality of the glass electrode (which is an ISE electrode based on the glass-membrane-potential, and not an ion-reversible electrode). This functionality must obviously be checked prior to use of cell (6). If the glass electrode in a nonaqueous solvent S was incapable of correct response, another  $H^+$ -selective-membrane must be singled out and characterized for use.

12. Some intervention in the rH-metric domain by such authoritative standardization bodies as, e.g., IUPAC and ISO, for appropriate guidelines and endorsements seems overdue and would be highly desirable.

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## REFERENCES

1. Bates R. G.: *Determination of pH – Theory and Practice*, 2nd ed. Wiley, New York 1973.
2. Perrin D. D., Dempsey B.: *Buffers for pH and Metal Ion*. Chapman & Hall, London 1974.
3. Covington A. K., Bates R. G., Durst R. A.: *Pure Appl. Chem.* **1985**, *57*, 531.
4. Mussini T., Covington A. K., Longhi P., Rondinini S.: *Pure Appl. Chem.* **1985**, *57*, 865; and references therein.
5. Rondinini S., Longhi P., Mussini P. R., Mussini T.: *Pure Appl. Chem.* **1987**, *59*, 1693.
6. Mussini P. R., Mussini T., Rondinini S.: *Pure Appl. Chem.* **1997**, *69*, 1007; and references therein.
7. Buck R. P., Rondinini S., Covington A. K., Baucke F. G. K., Brett C. M. A., Camoes M. F., Milton M. J. T., Mussini T., Naumann R., Pratt K. W., Spitzer P., Wilson G. S.: *Pure Appl. Chem.* **2002**, *74*, 2169.
8. Ives D. J. G., Janz G. J.: *Reference Electrodes – Theory and Practice*, pp. 362–364, 478–483. Academic Press, New York 1961.
9. Mussini P. R., Meyer G.: *GIT Fachz. Lab.* **1991**, *35*, 197.
10. Antonini D., Falcicola L., Mussini P. R., Mussini T.: *Ann. Chim. (Rome)* **2001**, *91*, 117.
11. Clark W. M., Cohen B.: *Public Health Rep. (U.S.)* **1923**, *38*, 933.
12. Clark W. M.: *Oxidation-Reduction Potentials of Organic Systems*. William & Wilkins Co., Baltimore (MD) 1960.
13. Pourbaix M.: *Thermodynamics of Dilute Aqueous Systems*, p. 38. Arnold, London 1949.
14. Pourbaix M.: *Atlas d'Equilibres Electrochimiques à 25 °C*, pp. 101–105. Gauthier-Villars, Paris 1963.
15. Longhi P., Mussini T., Orsenigo R., Rondinini S.: *J. Appl. Electrochem.* **1987**, *17*, 505.
16. Falcicola L., Mussini P. R., Mussini T.: *J. Solution Chem.* **2000**, *29*, 1199.
17. Mussini T., Pagella A.: *J. Chem. Eng. Data* **1971**, *16*, 49.
18. Bard A. J., Parsons R., Jordan J.: *Standard Potentials in Aqueous Solution*, p. 267. Marcel Dekker, New York 1985.
19. Veibel S.: *J. Chem. Soc.* **1923**, *123*, 2203.
20. Owen B. B.: *J. Am. Chem. Soc.* **1932**, *54*, 1758.
21. Ives D. J. G., Janz G. J.: *Reference Electrodes – Theory and Practice*, Chapters 2 and 10. Academic Press, New York 1961.
22. Bates R. G.: *Determination of pH – Theory and Practice*, 2nd ed., pp. 372–375. Wiley, New York 1973.
23. Ives D. J. G., Janz G. J.: *Reference Electrodes – Theory and Practice*, pp. 265–266. Academic Press, New York 1961.