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Medium Effects and Determination of Primary and Secondary Standards for pH Measurements in (Glycerol + Water) Solvent Media at Normal and Subzero Temperatures, With Characterization of Appropriate Salt Bridges[†]

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The primary and the secondary standards for the pH measurements in solvent media Z = (glycerol [G] + water [W]) at glycerol mass fractions w_G up to 0.4 and at temperatures from −10 °C to +40 °C have been determined in compliance with the IUPAC criteria. To this purpose, Harned's reversible cell {Pt|H_2|Primary Buffer + KCl in Z|AgCl|Ag|Pt} and Baucke's nonreversible cell {Pt|H_2|Buffer at pH_{PS} in Z|Salt Bridge in Z|Buffer at pH_{SS} in Z|H_2|Pt} were used, respectively. As a result, three primary standards (based on the "carbonate", the "equimolal phosphate", and the "phthalate" buffers) and three secondary standards (based on the "tetroxalate", the "tartrate", and the "unequimolal phosphate" buffers) are now available. Their internal consistency was ascertained through the linear pH dependence of the voltage of the cell {Pt|H_2 |Buffer at pH_{PS} [or pH_{SS}] in Z|NH_4Cl Bridge in Z|Reference Electrode}. These acquisitions enable the user to perform routine pH_X measurements by the regular operational cell {Reference Electrode|Salt Bridge in Z|Sample at pH_X or Standard at pH_{PS} [or pH_{SS}] in Z|Glass Electrode}, with preliminary calibration by the two-standard scheme or the multistandard scheme. As indispensable components to be selected for insertion in the above operational pH cell to abate the intervening liquid junction potentials, four salt bridges (NH_4Cl, RbCl, CsCl, and KCl in Z) have been characterized by the transference cell method: the most appropriate and recommended of them is the saturated NH_4Cl bridge. The comparability of pH scales in (glycerol + water) with the pH scale in pure water is discussed in terms of the relevant autoprotolysis constants pK_{AP} for the scale widths and of the primary medium effects of the H^+ transfer for the relative positions of zero-points of pH scales.

Introduction

In the domain of the physical chemistry and electrochemistry of acid−base equilibria, quite recently,[1] the IUPAC issued a key innovatory document (Recommendations 2002) which replaces the earlier recommendations[2] of 1985 in that it reassesses the basic pH rationale, the terminology, the methodology of establishing the pertinent reference solutions (pH standards), and the procedure of evaluation of the uncertainty budget of the latter ones. In short, this represents a conclusive manifesto for the primary and secondary pH standardization.

Although these key points apply to pH measurements in any solvent, the above document provides critical sets of primary (pH_{PS}) and secondary (pH_{SS}) standards for pH measurements in pure water only, because the pure aqueous medium was hitherto studied by far more extensively than any other medium, and thus the aqueous pH standardization can now be considered as firmly operational.

However, the situation is profoundly different in the domain of mixed solvents. In fact, the latter embraces a practically unlimited number of solvent systems, but regrettably, hitherto only 12 binary solvent systems (i.e., water + organic cosolvent) were explored,[3−9] besides the cases of pure formamide[10] and pure *N*-methylacetamide,[11] for the determination of the relevant primary or secondary standards.

Methodology of Determination of the pH Standards

Glycerol (relative permittivity $\varepsilon = 42.5$ at 298 K), the protic cosolvent chosen for the present research, has several interesting aspects especially in connection with such biomedical areas as the cryoconservation of clinical tissues. The aim of the present study is the implementation of the primary and secondary standardizations for pH measurements in the (glycerol (G) + water (W)) solvent system Z = G + W. This necessarily implies a parallel extended work (which is described in the subsequent paragraph) for the characterization of appropriate salt bridges in Z for the abatement of the liquid junction potentials arising between the sample solution and the reference electrode solution in the routine pH-measuring cell. The IUPAC document[1] prescribes that the primary standards, pH_{PS}, be determined exclusively by the "primary method" based on measuring the voltage E_1 of Harned's reversible cell

$$\mathrm{Pt|H_2\ (101.325\ kPa)|Primary\ Standard\ Buffer}\ (m_{PS}) + \mathrm{KCl}\ (m_{Cl})\mathrm{|AgCl|Ag|Pt} \quad (1)$$

whereas the secondary standards, pH_{SS}, should be determined by either of the nonreversible cells 2 or 3 shown below.

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$$\begin{gathered}\mathrm{Pt}|\mathrm{H}_2\ (101.325\ \mathrm{kPa})|\text{Primary Standard Buffer } (m_{\mathrm{PS}}) \\ |\text{Salt Bridge}| \\ \text{Secondary Standard Buffer } (m_{\mathrm{SS}})|\mathrm{H}_2\ (101.325\ \mathrm{kPa})|\mathrm{Pt} \quad (2)\end{gathered}$$

$$\begin{gathered}\mathrm{Pt}|\mathrm{H}^+\text{-sensing Glass Electrode} \\ |\text{Secondary Standard Buffer } (m_{\mathrm{SS}})|\mathrm{AgCl}|\mathrm{Ag}|\mathrm{Pt} \quad (3)\end{gathered}$$

In the nonreversible cell 2, sometimes referred to as Baucke's cell, both component electrodes are H^+-reversible, whereas the nonreversibility of cell 3 comes from the nonreversibility of the glass electrode, which is an ion-selective membrane electrode. The cell 2, where the secondary standard $\mathrm{pH}_{\mathrm{SS}}$ is compared to a selected primary standard $\mathrm{pH}_{\mathrm{PS}}$, can be used in two alternative configurations: (a) with the primary and the secondary buffer having the same nominal composition, $m_{\mathrm{PS}} = m_{\mathrm{SS}}$, thus resulting structurally in a symmetrical cell, or (b) with the primary and the secondary buffers having different compositions, thus resulting in an unsymmetrical cell. The scheme (b) has been used here. Of course, it is understood that the solvent used in all the above cells for the present investigation is Z = G + W.

Let us revert to Harned's cell 1, whose voltage E_1 can, in Nernstian terms, be expressed by the following equation

$$(E_1 - E°)/k = \log(m_{\mathrm{H}}\gamma_{\mathrm{H}}/m°) + \log(m_{\mathrm{Cl}}\gamma_{\mathrm{Cl}}/m°) = \mathrm{pH} + \log(m_{\mathrm{Cl}}/m°) + \log(\gamma_{\mathrm{Cl}}) \quad (4)$$

where $E°$ is the standard voltage of the cell (known from the literature[12]); γ represents the activity coefficients at molalities m of the single ions marked by subscripts without charge signs; $m° = 1\ \mathrm{mol{\cdot}kg^{-1}}$ is the reference molality; and $k = (\ln 10)RT/F$. All terms in eq 4 are known or measurable, except $\log(\gamma_{\mathrm{Cl}})$, which is computed by the IUPAC-endorsed Bates−Guggenheim equation in the form[3,4]

$$\log(\gamma_{\mathrm{Cl}}) = -A_{\mathrm{Z}}\cdot I^{1/2}/\{1 + 1.5(I\varepsilon_{\mathrm{W}}\rho_{\mathrm{Z}}/\varepsilon_{\mathrm{Z}}\rho_{\mathrm{W}})^{1/2}\} \quad (5)$$

where A_{Z} is the classical Debye−Hückel constant appropriate to the mixed solvent Z; I is the ionic strength of the cell

Table 1. Voltages E_1 (Normalized to p_{H2} = 101.325 kPa) of Harned's Reversible Cell 1 as a Function of Temperature T and Molality m_{KCl} of KCl Added to the Buffers "Equimolal Phosphate" and "Carbonate" of Fixed Compositions, in (Glycerol + Water) at Glycerol Mass Fraction (a) w_{G} = 0.20 and (b) 0.40[a]

(a)	w_{G} = 0.20				
T/K	268.15	273.15	283.15	298.15	313.15
$m_{\mathrm{KCl}}/(\mathrm{mol{\cdot}kg^{-1}})$	E_1/V	E_1/V	E_1/V	E_1/V	E_1/V
Buffer	Equimolal Phosphate: 0.025 $\mathrm{mol{\cdot}kg^{-1}}$ $\mathrm{Na_2HPO_4}$ + 0.025 $\mathrm{mol{\cdot}kg^{-1}}$ $\mathrm{KH_2PO_4}$				
0.0100	0.70773	0.71517	0.72663	0.74286	
0.0200	0.69399	0.69880	0.70842	0.72455	0.73954
0.0400		0.68466	0.69390	0.70771	0.72154
0.0700	0.66284	0.66770	0.67686	0.69011	0.70368
0.0850	0.66026	0.66561	0.67389	0.68681	0.69966
0.1000	0.65504	0.66104	0.67060	0.68349	0.69550
Buffer	Carbonate: 0.025 $\mathrm{mol{\cdot}kg^{-1}}$ $\mathrm{Na_2CO_3}$ + 0.025 $\mathrm{mol{\cdot}kg^{-1}}$ $\mathrm{NaHCO_3}$				
0.0050	0.90852	0.91597	0.92952	0.94924	0.96906
0.0100	0.89341	0.89922	0.91146	0.93058	0.95003
0.0200					0.93007
0.0400	0.85850	0.86463	0.87572	0.89338	0.91122
0.0500	0.85416	0.85959	0.87135	0.88889	0.90503
0.0699	0.84503	0.85052	0.86169	0.87863	0.89498
0.0912	0.83843	0.84484	0.85591	0.87176	0.88801
0.1000	0.83600	0.84218	0.85271	0.86885	0.88284
$E°$/V	0.22592	0.22377	0.21860	0.20951	0.19897
ε	84.17	82.17	78.32	72.88	67.81
$\rho/(\mathrm{kg{\cdot}dm^{-3}})$	1.0497	1.0497	1.0487	1.0451	1.0390
$A_Z/(\mathrm{kg^{1/2}{\cdot}mol^{-1/2}})$	0.55143	0.55606	0.56592	0.58247	0.60118
$10^8B_Z/(\mathrm{kg^{1/2}{\cdot}mol^{-1/2}{\cdot}nm^{-1}})$	3.4296	3.4392	3.4583	3.4877	3.5178

(b)	w_{G} = 0.40			
T/K	263.15	283.15	298.15	313.15
$m_{\mathrm{KCl}}/(\mathrm{mol{\cdot}kg^{-1}})$	E_1/V	E_1/V	E_1/V	E_1/V
Buffer	Equimolal Phosphate: 0.025 $\mathrm{mol{\cdot}kg^{-1}}$ $\mathrm{Na_2HPO_4}$ + 0.025 $\mathrm{mol{\cdot}kg^{-1}}$ $\mathrm{KH_2PO_4}$			
0.005	0.71551	0.73821	0.75567	0.77257
0.02	0.68326	0.70366	0.71954	0.73447
0.04	0.66606	0.68586	0.70057	0.71501
0.07	0.65248	0.67109	0.68454	0.69768
0.1	0.64330	0.66095	0.67428	0.68713
Buffer	Carbonate: 0.025 $\mathrm{mol{\cdot}kg^{-1}}$ $\mathrm{Na_2CO_3}$ + 0.025 $\mathrm{mol{\cdot}kg^{-1}}$ $\mathrm{NaHCO_3}$			
0.005	0.89345	0.92160	0.94238	0.96211
0.01	0.87800	0.90555	0.92518	0.94253
0.04	0.82239	0.86987	0.88758	0.90543
0.07	0.83308	0.85587	0.87339	0.88897
0.1	0.84488	0.84633	0.86239	0.87758
$E°$/V	0.21336	0.20315	0.19337	0.18188
ε	79.65	72.15	67.00	62.21
$\rho/(\mathrm{kg{\cdot}dm^{-3}})$	1.1050	1.1019	1.0973	1.0895
$A_Z/(\mathrm{kg^{1/2}{\cdot}mol^{-1/2}})$	0.63221	0.65614	0.67702	0.70058
$10^8B_Z/(\mathrm{kg^{1/2}{\cdot}mol^{-1/2}{\cdot}nm^{-1}})$	3.6515	3.6937	3.7267	3.7609

[a] Ancillary quantities taken or interpolated from the literature: standard emf's $E°$ of cell 1, together with relative permittivities ε and densities ρ of solvent mixtures [7,12,17,18] for calculations of Debye-Hückel constants A_{Z} and B_{Z}.

electrolyte; and ε and ρ are relative permittivities and densities of the components marked by subscripts.

From the emf E_2 of cell 2, the relevant expression for the secondary standard $\mathrm{pH_{SS}}$ is

$$\mathrm{pH_{SS}} = \mathrm{pH_{PS}} - E_2/k + E_{\mathrm{JR}} \qquad (6)$$

where the residual liquid junction potential E_{JR} may be taken as zero if the salt bridge is chosen appropriately. To this purpose, a search is essential to single out one or more alkali chlorides MCl that be equitransferent, namely, that have ionic transference numbers satisfying the condition $t_+ = t_- = 0.5$ as closely as possible.

Methodology for the Characterization of Appropriate Salt Bridges in the Present Solvent Mixtures

Since the required data pertaining to the (glycerol + water) media were hitherto lacking, a systematic study has been here performed by the transference cell method, which was recently reassessed critically by our research group.[13,14] This experimentation is based on voltage E_7 measurements on the transference cell 7

$$\mathrm{Ag|AgCl|MCl}\ (m_2)\|\mathrm{MCl}\ (m_1)|\mathrm{AgCl|Ag} \qquad (7)$$

combined with the parallel voltage E_{MAX} of the nontransference cell 8

$$\mathrm{Ag|AgCl|MCl}\ (m_2)|\mathrm{MAmalgam}|\mathrm{MCl}\ (m_1)|\mathrm{AgCl|Ag} \qquad (8)$$

In fact, for the relevant transference number $t_{\mathrm{M+}}$, the following thermodynamic equation holds

$$t_{\mathrm{M+}} = \mathrm{d}E_7/\mathrm{d}E_{\mathrm{MAX}} \qquad (9)$$

which is in turn linked with the following pair of interrelated equations

$$t_{\mathrm{M+}} + t_{\mathrm{Cl^-}} = 1 = \mathrm{d}E_7/\mathrm{d}E_{\mathrm{MAX}} + \mathrm{d}E_{12}/\mathrm{d}E_{\mathrm{MAX}} \qquad (10)$$

$$E_7 + E_{12} = E_{\mathrm{MAX}} \quad \text{and} \quad \mathrm{d}E_7 + \mathrm{d}E_{12} = \mathrm{d}E_{\mathrm{MAX}} \qquad (11)$$

where E_{12} is the voltage of the cell 12:

$$\mathrm{MAmalgam|MCl}\ (m_1)\|\mathrm{MCl}\ (m_2)|\mathrm{MAmalgam} \qquad (12)$$

Details for the application of these equations are given in the Results and Discussion section.

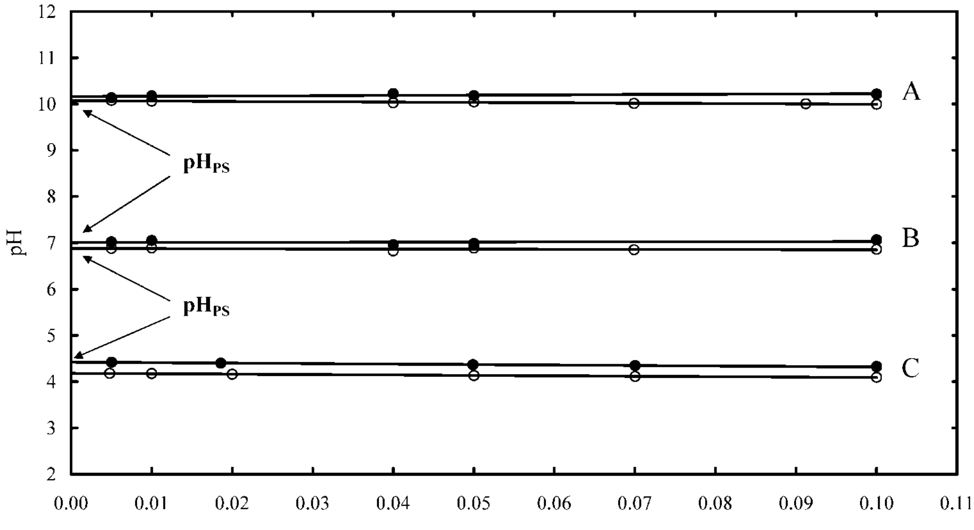

Figure 1. Extrapolation to $m_{\mathrm{KCl}} = 0$ for the pH values based on eqs 4 and 5 to obtain the primary standard values $\mathrm{pH_{PS}}$ at 298.15 K pertaining to the carbonate (lines A), equimolal phosphate (lines B), and phthalate (lines C) buffers in (glycerol + water) for glycerol mass fractions $w_G = 0.20$ (empty points) and $w_G = 0.40$ (full points), respectively.

Table 2. pH Standards at Various Temperatures *T* and Glycerol Mass Fractions w_G in (Glycerol + Water), with Corresponding Expanded Uncertainties[1] U[a]

			T/K					
buffers	type of pH standard	w_G	263.15	268.15	273.15	283.15	298.15	313.15
0.05 mol·kg^{-1} $KH_3C_4O_8 \cdot 2H_2O$[b]	$\mathrm{pH_{SS}} \pm U$	0.20		1.745 ± 0.038	1.709 ± 0.025	1.669 ± 0.048	1.733 ± 0.019	1.760 ± 0.026
		0.40	1.886 ± 0.024			1.856 ± 0.018	1.975 ± 0.018	1.888 ± 0.025
sat. $KHC_4H_4O_6$[c]	$\mathrm{pH_{SS}} \pm U$	0.20		3.881 ± 0.039	3.837 ± 0.025	3.764 ± 0.039	3.811 ± 0.018	3.797 ± 0.026
		0.40	4.149 ± 0.022			4.074 ± 0.018	4.024 ± 0.018	4.069 ± 0.025
0.05 mol·kg^{-1}$KHC_8H_4O_4$[d](*)	$\mathrm{pH_{PS}} \pm U$	0.20		4.164 ± 0.012	4.157 ± 0.012	4.156 ± 0.012	4.172 ± 0.012	4.201 ± 0.012
		0.40	4.434 ± 0.014			4.406 ± 0.012	4.420 ± 0.012	4.451 ± 0.012
0.025 mol·kg^{-1} Na_2HPO_4 + 0.025 mol·kg^{-1} KH_2PO_4[e]	$\mathrm{pH_{PS}} \pm U$	0.20		6.956 ± 0.030	6.955 ± 0.030	6.915 ± 0.029	6.890 ± 0.026	6.880 ± 0.027
		0.40	7.183 ± 0.016			7.088 ± 0.011	7.068 ± 0.013	7.065 ± 0.014
0.03043 mol·kg^{-1} Na_2HPO_4 + 0.008695 mol·kg^{-1} KH_2PO_4[f]	$\mathrm{pH_{SS}} \pm U$	0.20		7.604 ± 0.039	7.547 ± 0.025	7.457 ± 0.047	7.463 ± 0.018	7.382 ± 0.025
		0.40	7.698 ± 0.024			7.642 ± 0.018	7.624 ± 0.018	7.601 ± 0.025
0.025 mol·kg^{-1} Na_2CO_3 + 0.025 mol·kg^{-1}$NaHCO_3$[g]	$\mathrm{pH_{PS}} \pm U$	0.20		10.420 ± 0.018	10.345 ± 0.018	10.219 ± 0.020	10.073 ± 0.017	9.965 ± 0.017
		0.40	10.596 ± 0.019			10.357 ± 0.017	10.225 ± 0.017	10.110 ± 0.017

[a] Data for the phthalate buffer (*) are recalculated from ref 7. [b] Buffers' denominations: Tetroxalate. [c] Tartrate. [d] Phthalate. [e] Equimolal phosphate. [f] Unequimolal phosphate. [g] Carbonate.

Table 3. Voltage Values E_2 of Cell 2 for Three Secondary Standard Buffers Measured against Three Primary Standard Buffers at Different Temperatures T and Glycerol Mass Fractions w_G in (Glycerol + Water)

		$w_G = 0.20$			$w_G = 0.40$		
		primary buffers			primary buffers		
		E_2/V			E_2/V		
secondary buffers	T/K	phthalate	equimolal phosphate	carbonate	phthalate	equimolal phosphate	carbonate
tetroxalate	263.15				0.13501	0.27619	0.45411
	268.15	0.13318	0.27688	0.45943			
	273.15	0.13279	0.28595	0.46557			
	283.15	0.13698	0.29366	0.48769	0.14384	0.29349	0.47743
	298.15	0.14418	0.30654	0.49259	0.14475	0.30200	0.48666
	313.15	0.15205	0.31910	0.50716	0.15858	0.32118	0.51344
tartrate	263.15				0.01672	0.15790	0.33582
	268.15	0.01830	0.16200	0.34455			
	273.15	0.01750	0.17066	0.35028			
	283.15	0.01851	0.17519	0.36922	0.01933	0.16898	0.35292
	298.15	0.02124	0.18360	0.36965	0.02356	0.18081	0.36547
	313.15	0.02548	0.19253	0.38059	0.02307	0.18567	0.37793
unequimolal phosphate	263.15				−0.16846	−0.02728	0.15064
	268.15	−0.17857	−0.03487	0.14768			
	273.15	−0.18361	−0.03044	0.14918			
	283.15	−0.18830	−0.03160	0.16240	−0.18113	−0.03148	0.15246
	298.15	−0.19481	−0.03245	0.15360	−0.18945	−0.03220	0.15246
	313.15	−0.19730	−0.03025	0.15781	−0.19639	−0.03379	0.15847

Table 4. Voltages E_{13} of Cell 13 in (Glycerol + Water) at Various Glycerol Mass Fractions w_G and Various Temperatures T and Constants of the Straight Line $E_{13} = \alpha + k'$ pH, Where α = Working Potential of the Calomel Reference Electrode

	T/K	263.15	268.15	273.15	283.15		298.15		313.15	
	w_G	0.4	0.2	0.2	0.2	0.4	0.2	0.4	0.2	0.4
type of pH standard	buffers	E_{13}/V	E_{13}/V	E_{13}/V	E_{13}/V	E_{13}/V	E_{13}/V	E_{13}/V	E_{13}/V	E_{13}/mV
pH_{SS}	0.05 mol·kg^{-1} $KH_3C_4O_8\cdot 2H_2O$[a]	0.35044	0.35501	0.35440	0.35030	0.34537	0.34770	0.34682	0.34714	0.33989
pH_{SS}	sat. $KHC_4H_4O_6$[b]	0.46873	0.46989	0.46969	0.46877	0.46988	0.47064	0.46801	0.47371	0.47540
pH_{PS}	0.05 mol·kg^{-1} $KHC_8H_4O_4$[c]	0.48545	0.48819	0.48719	0.48728	0.48921	0.49188	0.49157	0.49919	0.49847
pH_{PS}	0.025 mol·kg^{-1} Na_2HPO_4 + 0.025 mol·kg^{-1} KH_2PO_4[d]	0.62663	0.63189	0.64035	0.64396	0.63886	0.65424	0.64882	0.66624	0.66107
pH_{SS}	0.03043 mol·kg^{-1} Na_2HPO_4 + 0.008695 mol·kg^{-1} KH_2PO_4[e]	0.65391	0.66676	0.67079	0.67556	0.67034	0.68669	0.68102	0.69649	0.69486
pH_{PS}	0.025 mol·kg^{-1} Na_2CO_3 + 0.025 mol·kg^{-1} $NaHCO_3$[f]	0.80455	0.81444	0.81997	0.83799	0.82280	0.84029	0.83348	0.85430	0.85333
	α/V	0.2529 ± 0.0010	0.2651 ± 0.0019	0.2628 ± 0.0012	0.2531 ± 0.0027	0.2413 ± 0.0003	0.2455 ± 0.0008	0.2306 ± 0.0006	0.2390 ± 0.0011	0.2213 ± 0.010
	k'/V	0.05211 ± 0.00015	0.05279 ± 0.00029	0.05400 ± 0.00019	0.05629 ± 0.00043	0.05614 ± 0.00005	0.05912 ± 0.00012	0.05904 ± 0.00010	0.06189 ± 0.00017	0.06239 ± 0.00015
	r^2	0.99997	0.99988	0.99997	0.99978	0.999997	0.99998	0.99999	0.99997	0.99998
	$k = (\ln 10)RT/F$/V	0.052215	0.053207	0.054199	0.056183		0.059160		0.062136	

[a] Buffers' denominations: Tetroxalate. [b] Tartrate. [c] Phthalate. [d] Equimolal phosphate. [e] Unequimolal phosphate. [f] Carbonate.

An important point is the verification of the internal consistency of the found primary pH_{PS} or/and secondary (pH_{SS}) standards. This verification requires measuring the voltage E_{13} of cell 13

$$\mathrm{Pt|H_2\ (101.325\ kPa)|pH_{PS}\ or/and\ pH_{SS}\ Solution|Salt\ Bridge|Reference\ Electrode} \quad (13)$$

where the whole sequence of the standards in question is to be tested, and it rests on the following rationale: if the found standards had exact mutual consistency (ideal conditions, with perfect salt bridge), then plotting E_{13} vs pH_{PS} (or pH_{SS}) should produce a straight line of theoretical Nernstian slope $k = (\ln 10)RT/F$. Under real conditions of experimental errors, of course, the practical slope k' could somewhat differ from the theoretical one. As shown later, in this work, the observed k' values are in good accord with the theoretical value k, thus denoting an excellent degree of such consistency, which is beneficial to the user's confidence.

Experimental

The silver/silver chloride electrodes in cells 1 and 7 were prepared according to the bielectrolytic type.[15] The hydrogen electrodes in cells 1 and 2 were prepared as in our previous works in aqueous−organic media.[7,8] The solutions were prepared by mass from redistilled deionized water and the following chemicals: potassium tetroxalate (Fluka, > 99.5 %), potassium hydrogen tartrate (Aldrich, 99 %), potassium hydrogen phthalate (Merck, DKD), disodium hydrogen phosphate and potassium dihydrogen phosphate (Carlo Erba, 99.5 %), sodium hydrogen carbonate and sodium carbonate (Fluka, > 99.5 %), and glycerol (Fluka, > 99.5 %). The measurements of cell voltages were performed by a 619 Keithley differential electrometer of input impedance higher than 10^{14} Ω. The uncertainty of voltage measurements was ± 0.01 mV. The thermostatic apparatus was described earlier[16] and ensured a temperature stability of ± 0.02 K. To reach subzero temperatures, a type EN 850 Neslab flow-through cooler was used.

Results and Discussion

Tables 1a and 1b report the values of the voltage E_1 of Harned's cell 1 measured over the temperature range from −5 °C to +40 °C, in (glycerol + water) at glycerol mass fractions $w_G = 0.20$ and $w_G = 0.40$, respectively, for the two primary standard buffers of fixed compositions (0.025 mol·kg^{-1}

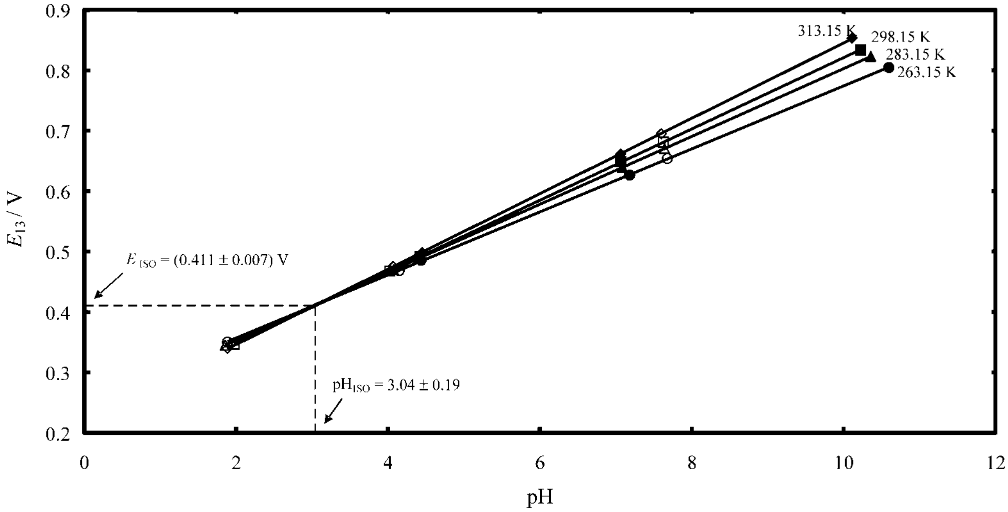

Figure 2. Verification of the internal consistency of the pH standards in (glycerol + water) in terms of the linear relation of the voltage E_{13} vs the group of pH_{PS} (full points) and pH_{SS} (empty points) at various temperatures explored and identification of the "isopotential pH" point of coordinates pH_{ISO} and E_{ISO}, at glycerol mass fraction $w_G = 0.4$ (●,○, 263.15 K; ▲,△, 283.15 K; ■,□, 298.15 K; ◆,◇, 313.15 K).

Na_2HPO_4 + 0.025 $mol\cdot kg^{-1}$ $KHPO_4$) ["equimolal phosphate buffer"] and (0.025 $mol\cdot kg^{-1}$ Na_2CO_3 + 0.025 $mol\cdot kg^{-1}$ $NaHCO_3$) ["carbonate buffer"], respectively, but with varying molalities m_{Cl} of added KCl. For convenience, the same tables quote the ancillary quantities (taken from the literature) needed by eqs 4 and 5 for the computation of the pH values at each glycerol mass fraction explored, namely, the standard voltage values $E^{\circ 12}$ and the relative permittivities ε and densities ρ of the mixed solvents (for the calculation of the pertinent values of the Debye−Hückel constant A_Z).[7,12,17,18]

The pH values calculated from the combined eqs 4 and 5 show slight differences due to ionic interactions between KCl and the relevant buffer. To remove this effect, these pH values are plotted against the corresponding molalities m_{Cl} and the pH value extrapolated to $m_{Cl} = 0$ is finally assigned the qualification of primary standard pH_{PS} (see Figure 1). The pH_{PS} values for the explored buffers mentioned above at each temperature and solvent composition are quoted in Table 2, together with the pertinent values of expanded uncertainty. These expanded uncertainties U have been calculated according to the uncertainty budget procedure suggested by the IUPAC document,[1] which focuses the further usefulness of making the found pH_{PS}'s traceable to SI but discusses the connected problem of the uncertainty contribution brought about by use of the nonthermodynamic Bates−Guggenheim convention 5. The IUPAC document concludes estimating this particular contribution to amount to 0.01 in pH. Therefore, for the traceability to SI, each U figure quoted in Table 2 includes that additive 0.01 contribution. For comparison and completion reasons, in Table 2 are also quoted the pH_{PS} values pertaining to the 0.05 $mol\cdot kg^{-1}$ potassium hydrogen phthalate (KHPh) buffer, as determined in a recent preliminary work,[7] with expanded uncertainties now recalculated in terms of the above IUPAC document.

The voltage E_2 values of cell 2 for the determination of the secondary standards pH_{SS} are quoted in Table 3. To this purpose, the unequimolal phosphate, the tartrate, and the tetroxalate buffers were studied versus the three primary standards pH_{PS} offered by the carbonate, the equimolal phosphate, and the phthalate buffers, used as fixed references in cell 2 at each temperature, employing the saturated solution of NH_4Cl as the most appropriate salt bridge in the (glycerol + water) solvent mixtures explored. For each of the three secondary buffers cited above, the pertinent pH_{SS} value has been determined versus each of the three primary buffers of known pH_{PS} (obviously at each temperature T and each glycerol mass fraction w_G). For the three pH_{SS} values thus computed by eq 6, the weighted mean has been quoted in Table 2, together with the pertinent expanded uncertainty U, for a total of 30 cases.

Once the three primary standards pH_{PS} and three secondary standards pH_{SS} above have been acquired, the verification of their internal consistency is to be performed through the voltage E_{13} of cell 13, the values of which are quoted in Table 4. In cell 13, the reference electrode was a calomel electrode having a built-in NH_4Cl salt bridge. The slopes of the E_{13} vs pH_{PS} straight lines are in good agreement with the theoretical values $k = (\ln 10)RT/F$ at each temperature of experiment. The very small $(k' - k)$ deviations observed are due to overlapping of pH-dependent residual liquid junction potentials, as was discussed in a recent paper.[19] Figure 2, which visualizes altogether all the six pH standards determined hitherto in (glycerol + water), provides evidence of their excellent mutual consistency. The coordinates of the intersection point of these E_{13} vs pH isotherms,[20,21] which defines the "isopotential pH" point, turn out to be: $pH_{ISO} = (3.01 \pm 0.11)$ and $E_{ISO} = (0.425 \pm 0.006)$ V at the glycerol mass fraction $w_G = 0.20$ and $pH_{ISO} = (3.04 \pm 0.13)$ and $E_{ISO} = (0.411 \pm 0.007)$ V at $w_G = 0.40$, respectively (cf. Figure 2).

To perform correct pH_X measurements in the given solvent Z by the regular cell 14

$$\text{Reference Electrode}|\text{Salt Bridge}$$
$$|\text{Sample at } pH_X \text{ or Standard at } pH_{PS}|H^+\text{-Sensor} \quad (14)$$

related to the well-known operational equation

$$pH_X = pH_{PS} - (E_X - E_{PS})/k' \qquad (15)$$

(where k' is the practical slope factor and the residual liquid junction potential is ignored[1]), the availability of accurate pH_{PS} (or pH_{SS}) standards in Z is a necessary but not sufficient condition. The complementary key condition is the availability of appropriately equitransferent[22] salt bridges in the same solvent Z for insertion in cell 14 between the sample solution and the reference electrode for the abatement of the intervening liquid junction potentials at the | junction. The known binary salts usable in *aqueous* solutions as salt bridges are the group of the halides or nitrates of rubidium, cesium, ammonium, and

Table 5. Voltages E_7 of Cell 7 at 298.15 K, and Corresponding E_{MAX}, as Functions of the Variable Molalities m_1 of MCl (with Corresponding Mean Molal Activity Coefficients γ_1) in (Glycerol + Water) at Glycerol Mass Fraction w_G = (a) 0.20 and (b) 0.40, for a Fixed Molality m_2 = 0.1 mol·kg^{-1} (with Corresponding γ_2 Values), with ε = 72.88 and ρ = 1.0451 kg·dm^{-3}[a]

(a)	$w_G = 0.20$						
LiCl	$t^\circ_{\mathrm{Li}+} = (0.322 \pm 0.009)$; $\gamma_2 = 0.747$; $a_0 = 0.43$ nm						
m_1/(mol·kg^{-1})	0.01	0.02	0.03	0.04	0.05	0.07	0.10
E_7/V	0.035380	0.026346	0.019407	0.014623	0.011837	0.006966	0.00
E_{MAX}/V	0.109330	0.075779	0.056404	0.042771	0.032275	0.016531	0.00
γ_1	0.890	0.854	0.831	0.812	0.797	0.773	0.747
NaCl	$t^\circ_{\mathrm{Na}+} = (0.391 \pm 0.003)$; $\gamma_2 = 0.742$; $a_0 = 0.40$ nm						
E_7/V	0.042967	0.030410	0.022460	0.016980	0.014343	0.007100	0.00
E_{MAX}/V	0.109035	0.075471	0.056203	0.042601	0.032125	0.016461	0.00
γ_1	0.889	0.853	0.828	0.809	0.794	0.769	0.742
KCl	$t^\circ_{\mathrm{K}+} = (0.494 \pm 0.005)$; $\gamma_2 = 0.740$; $a_0 = 0.38$ nm						
E_7/V	0.053800	0.036518	0.026865	0.020146	0.015075	0.007600	0.00
E_{MAX}/V	0.108962	0.075464	0.056130	0.042561	0.032083	0.016448	0.00
γ_1	0.888	0.852	0.828	0.809	0.793	0.768	0.740
NH_4Cl	$t^\circ_{\mathrm{NH4}^+} = (0.495 \pm 0.003)$; $\gamma_2 = 0.740$; $a_0 = 0.43$ nm						
E_7/V	0.054210	0.037685	0.028071	0.021688	0.016145	0.009207	0.00
E_{MAX}/V	0.108950	0.075464	0.056130	0.042539	0.032096	0.016440	0.00
γ_1	0.888	0.852	0.828	0.808	0.793	0.768	0.740
RbCl	$t^\circ_{\mathrm{Rb}+} = (0.505 \pm 0.008)$; $\gamma_2 = 0.740$; $a_0 = 0.39$ nm						
E_7/V	0.055225	0.039024	0.029534	0.022891	0.017328		0.00
E_{MAX}/V	0.108950	0.075463	0.056116	0.032072	0.032072		0.00
γ_1	0.888	0.852	0.828	0.809	0.793		0.740
CsCl	$t^\circ_{\mathrm{Cs}+} = (0.481 \pm 0.005)$; $\gamma_2 = 0.739$; $a_0 = 0.38$ nm						
E_7/V	0.052356	0.036379	0.027206	0.019916	0.016153	0.007936	0.00
E_{MAX}/V	0.108841	0.075375	0.056037	0.042461	0.032049	0.016447	0.00
γ_1	0.888	0.852	0.827	0.808	0.792	0.767	0.739
(b)	$w_G = 0.40$						
LiCl	$t^\circ_{\mathrm{Li}+} = (0.315 \pm 0.005)$; $\gamma_2 = 0.717$; $a_0 = 0.43$ nm						
m_1/(mol·kg^{-1})	0.01	0.02	0.03	0.04	0.05	0.07	0.10
E_7/V	0.033714	0.023225	0.016577	0.012312	0.009230	0.004367	0.00
E_{MAX}/V	0.108153	0.074898	0.055716	0.042240	0.031857	0.016313	0.00
γ_1	0.874	0.835	0.808	0.788	0.772	0.746	0.717
NaCl	$t^\circ_{\mathrm{Na}+} = (0.397 \pm 0.008)$; $\gamma_2 = 0.712$; $a_0 = 0.39$ nm						
E_7/V	0.043183	0.030481	0.022918	0.018565		0.007529	0.00
E_{MAX}/V	0.107838	0.074619	0.055494	0.042051		0.016223	0.00
γ_1	0.873	0.833	0.806	0.785		0.741	0.712
KCl	$t^\circ_{\mathrm{K}+} = (0.493 \pm 0.008)$; $\gamma_2 = 0.717$; $a_0 = 0.38$ nm						
E_7/V	0.054070	0.037134	0.028724	0.021890	0.016988	0.010008	0.00
E_{MAX}/V	0.107588	0.074423	0.055324	0.041900	0.031585	0.016162	0.00
γ_1	0.872	0.831	0.805	0.783	0.765	0.738	0.708
NH_4Cl	$t^\circ_{\mathrm{NH4}^+} = (0.501 \pm 0.005)$; $\gamma_2 = 0.710$; $a_0 = 0.39$ nm						
E_7/V	0.054008	0.038126	0.028146	0.022161	0.016535	0.008618	0.00
E_{MAX}/V	0.107723	0.074534	0.055415	0.041973	0.031637	0.016223	0.00
γ_1	0.872	0.832	0.805	0.784	0.767	0.740	0.710
RbCl	$t^\circ_{\mathrm{Rb}+} = (0.499 \pm 0.003)$; $\gamma_2 = 0.710$; $a_0 = 0.39$ nm						
E_7/V	0.053690	0.036587	0.027497		0.015260	0.007780	0.00
E_{MAX}/V	0.107707	0.074534	0.055410		0.031600	0.016183	0.00
γ_1	0.872	0.832	0.805		0.767	0.740	0.710
CsCl	$t^\circ_{\mathrm{Cs}+} = (0.487 \pm 0.007)$; $\gamma_2 = 0.710$; $a_0 = 0.39$ nm						
E_7/V	0.052841	0.037011	0.027550	0.022161	0.016535	0.008618	0.00
E_{MAX}/V	0.107717	0.074516	0.055384	0.041951	0.031638	0.016197	0.00
γ_1	0.872	0.832	0.805	0.784	0.767	0.740	0.710

[a] Also quoted the pertinent limiting cation transference numbers $t^\circ_{\mathrm{M}+}$.

potassium, plus the lithium sulfate. Therefore, to single out and characterize salt bridges of appropriate level of equitransference in (glycerol + water), the series of alkali chlorides MCl has here been tested through measurements of the emf E_7 of the transference cell 7, whose electrodes are reversible to the anion Cl^-, at various MCl molalities m_1 up to 0.2 mol·kg^{-1} but with fixed m_2, to obtain the transference numbers $t_{\mathrm{M}+}$ of the corresponding cation M^+ at molality m_1. The measured E_7

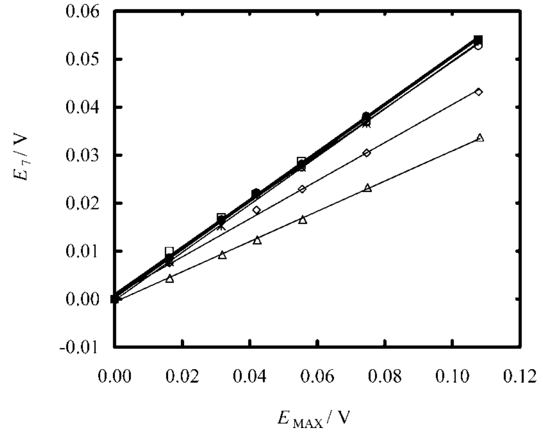

Figure 3. Linear E_7 vs E_{MAX} relationships for the determination of the cation transference numbers $t_{M+} = dE_7/dE_{MAX}$ (at 298.15 K and glycerol mass fraction $w_G = 0.40$) for the alkali chlorides MCl, with NH_4Cl featuring the closest approach to the equitransference condition ($t_{M+} = t_{Cl^-} = 0.5$). (△, Li^+; ◇, Na^+; □, K^+; *, Rb^+; ●, NH_4^+; ○, Cs^+).

values are to be seen in Tables 5a and 5b. The basic equation, related with eqs 9, 10, and 11, is[13,14]

$$dE_7/dE_{MAX} = t_{M+} - \tau_Z M_Z m_1 = a - Q(m_1\gamma_1)^{2kb} \quad (16)$$

where M_Z is the molar mass; τ_Z is the transport number of the solvent Z = (glycerol + water); and Q, a, and b are constants. Besides E_7, eq 16 requires the corresponding emf E_{MAX} of the nontransference cell 8, for the same molality pair ($m_2 > m_1$) of cell 7. The Nernstian expression of E_{MAX} with MCl electrolytes is

$$E_{MAX} = 2k \log(m_2\gamma_2/m_1\gamma_1) \quad (17)$$

and we have anyway $E_7 < E_{MAX}$. Evidently, E_{MAX} need not be measured if the relevant mean molal activity coefficients γ can be calculated as a function of MCl molality. This has been done here, within the above molality range, by use of the Debye−Hückel equation in the form

$$\log \gamma = -A_Z m^{1/2}/(1 + a_0 B_Z m^{1/2}) - \log(1 + 2mM_Z) \quad (18)$$

where for the calculation of the temperature-dependent constants A_Z and B_Z the ancillary data of relative permittivity ε_Z and density ρ_Z are quoted in Tables 1a and 1b, and for the ion-size parameter a_0 of each MCl, the same value generally used in water has been adopted. The related calculation of the sought t_{M+}s based on the joint eqs 16, 17, and 18 is rather insensitive to even conspicuous changes in a_0. At infinite dilution ($m_1 = 0$), from eq 16 we obtain the limiting transference number $t°_{M+}$

$$\lim_{m1=0}(dE_7/dE_{MAX}) = a = t°_{M+} \quad (19)$$

For all of the alkali halides explored, the experimental E_7 vs E_{MAX} relations are linear, as visualized in Figure 3, and their limiting slopes directly give the pertinent $t°_{M+}$ values. The result is that the alkali halides having the cation transference number sufficiently close to 0.5 so as to warrant their use as dependable salt bridges for pH or pI on measurement applications in (glycerol + water) are NH_4Cl, RbCl, CsCl, and KCl. This feature is rather similar to the one observed in pure water medium; however, looking over, in (glycerol + water), it is NH_4Cl that behaves best, and it has been preferred for use in the present work.

Medium Effects and Conclusive Remarks on Comparability of pH Scales in the Different Solvents Studied

Now, since six pH standards and four salt bridges have been characterized, the implementation of the routine practice of pH_X measurements by the regular cell 14 in (glycerol + water) media is achieved, including the possibility of performing the two-standard calibration (bracketing standards technique) or the multistandards calibration of the pH sensor unit.[1] However, as was shown in earlier monographs,[23−26] these pH_X values as well as the related standards pH_{PS} (or pH_{SS}) are just self-consistent in the specific (glycerol + water) solvent system considered, exactly as are the aqueous pH_X and pH_{PS} values in the specific water solvent: in other words, there is no thermodynamic intercomparability between different solvent systems. This fact is due to the *primary medium effect* [27,28] on the H^+ cation, namely, the standard Gibbs energy change $(\Delta G°_{H^+})_{W\to Z}$ accompanying the transfer of the single H^+ from the (*hyp.* $m_{H+} = 1$ in W) standard state in water to the (*hyp.* $m_{H+} = 1$ in Z) standard state in solvent Z, which is a nonthermodynamic quantity not amenable to experiment but only estimatable through extrathermodynamic assumptions. This quantity is related to the so-called activity coefficient of H^+ transfer,[23−26] $(\gamma^t_{H^+})_{W\to Z}$ and to the standard absolute potentials of the hydrogen electrode, $E°_{H2(Abs)}$, in the respective solvents W and Z, by the following equation

$$\{[E°_{H_2(Abs)}]_W - [E°_{H_2(Abs)}]_Z\}/k = -\log(\gamma^t_{H+})_{W\to Z} = (\Delta G_{oH+})_{W\to Z}/(2.303RT) = \Delta pH \quad (20)$$

where ΔpH is the algebraically additive correction to the $(pH_X)_Z$ value measured in solvent Z to obtain an "intersolvental" $[(pH_X)^* = (pH_X)_Z + \Delta pH]$ value physically comparable[23−26] with a $(pH_X)_W$ value in water W. Evidently this correction must be equally applied to the standard pH_{PS} or pH_{SS} values in Z to achieve the above intercomparability. Although reasonable ΔpH estimates for lower alcohols and diols are available in the literature,[23−26] regrettably, no such data were published hitherto for glycerol nor for (glycerol + water) solvents, although reasoning by analogy with alcohols and diols, one should guess such ΔpH to lie around $-(4 \pm 1)$.

Another intercomparability problem is that of the nominal width or range of pH scale in solvent Z,[23−26] which is defined as $pK_{AP} = -\log K_{AP}$, where K_{AP} is the autoprotolysis constant of solvent Z at 298.15 K. Unlike the primary medium effect on H^+, pK_{AP} is a thermodynamically defined quantity well amenable to experiment, and the values of pK_{AP} required for the present glycerol + water mixtures are available from the literature:[29−31] $pK_{AP} = 13.6$ and 13.4 at glycerol mass fractions $w_G = 0.20$ and 0.40, respectively. Therefore, looking over, if the above conservative hypotheses about ΔpH values are accepted, in terms of "intersolvental" pH* values for comparability with the aqueous scale, upon correction for the primary medium effect for the H^+ transfer, in both cases of $w_G = 0.20$ and $w_G = 0.40$ the resulting scales would range from about −4 to about +13.5, with only partial overlapping to the 0 to +14 aqueous pH scale.

Literature Cited

(1) 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. Measurement of pH. Definition, standards, and procedures: (IUPAC Recommendations 2002). *Pure Appl. Chem.* **2002**, *74*, 2169–2200.

(2) Covington, A. K.; Bates, R. G.; Durst, R. A. Definition of pH scales, standards, reference values, measurement of pH and related terminology. *Pure Appl. Chem.* **1985**, *57*, 531–542.

(3) Mussini, T.; Covington, A. K.; Longhi, P.; Rondinini, S. Criteria for standardization of pH measurements in organic solvents and water + organic solvent mixtures of moderate to high permittivities. *Pure Appl. Chem.* **1985**, *57*, 865–876.

(4) Rondinini, S.; Mussini, P. R.; Mussini, T. Reference value standards and primary standards for pH measurements in organic solvents and water + organic solvent mixtures of moderate to high permittivities. *Pure Appl. Chem.* **1987**, *59*, 1549–1560.

(5) Rondinini, S.; Mussini, P. R.; Mussini, T. Reference value standards and primary standards for pH measurements in D_2O and aqueous-organic solvent mixtures: new accessions and assessments. *Pure Appl. Chem.* **1997**, *69*, 1007–1014.

(6) Barbosa, J.; Barrón, D.; Butí, S.; Marqués, I. Assignment of pH_S values of reference buffer solutions for standardization of potentiometric sensors in THF-water. *Polyhedron* **1999**, *18*, 3361–3367.

(7) Falciola, L.; Mussini, P. R.; Mussini, T. Ionization constants of o-phthalic acid and standard pH values of potassium hydrogen phthalate buffer solutions in (glycerol + water) solvent mixtures at normal and subzero temperatures. *J. Solution Chem.* **2000**, *29*, 1199–1210.

(8) Antonini, D.; Falciola, L.; Mussini, P. R.; Mussini, T. Medium effects, comparability and predictability of pH-standards in aqueous-organic solvents isodielectric with water: behaviours of the (ethylene carbonate + water) and (propylene carbonate + water) systems. *J. Electroanal. Chem.* **2001**, *503*, 153–158.

(9) Falciola, L.; Mussini, P. R.; Mussini, T.; Rossi, M. A determination of standard potentials and related primary pH standards in the 50 mass percent (N-Methyl-2-Pyrrolidinone + Water) mixture at various temperatures. *J. Solution Chem.* **2007**, *36*, 1037–1046.

(10) Falciola, L.; Mussini, P. R.; Mussini, T.; Pelle, P. Determination of primary and secondary standards and characterization of appropriate salt bridges for pH measurements in formamide. *Anal. Chem.* **2004**, *76*, 528–535.

(11) Dumitrel, D.; Falciola, L.; Liotto, M.; Mussini, P. R.; Mussini, T.; Rossi, M. Determination of primary and secondary standards for pH measurements in N-Methylacetamide and its 0.50 mass fraction in admixture with water, with characterization of appropriate salt bridges. *J. Chem. Eng. Data* **2007**, *52*, 1595–1602.

(12) Falciola, L.; Mussini, P. R.; Mussini, T. Thermodynamics of the cell $Pt|H_2(p)|HCl\ (m)|AgCl|Ag$ and primary medium effects upon HCl in (glycerol+ water) solvent. *J. Chem. Thermodyn.* **2001**, *33*, 499–512.

(13) Mussini, P. R.; Mussini, T. Recent advances in the electromotive force method for determining transference numbers of electrolytes and characterizing new salt bridges. *J. Appl. Electrochem.* **1998**, *28*, 1305–1311.

(14) Mussini, P. R.; Mussini, T. An alternative methodology for determining transport parameters of electrolytes in mixed solvents from concentration cells, without prior knowledge of activity coefficients. *Electrochem. Commun.* **2000**, *2*, 108–111.

(15) Ives, D. J. G.; Janz, G. J. *Reference Electrodes−Theory and Practice*; Academic Press: New York, 1961; p 203.

(16) Mussini, T.; Pagella, A. Standard potentials of the calcium amalgam electrode at various temperatures, with related thermodynamic functions. *J. Chem. Eng. Data* **1971**, *16*, 49–52.

(17) Åkerlöf, G. Dielectric constants of some organic solvent-water mixtures at various temperatures. *J. Am. Chem. Soc.* **1932**, *54*, 4125–4139.

(18) Janz, G. J.; Tomkins, R. P. T. *Nonaqueous Electrolytes Handbook*; Academic Press: New York, 1972; Vol. 1, p 99.

(19) Falciola, L.; Mussini, P. R.; Mussini, T. Effect of the salt-bridge choice on the response of an ion selective electrode cell. *Ann. Chim. (Rome)* **2001**, *91*, 667–670.

(20) Covington, A. K. In *Ion-Selective Electrodes*; Durst, R. A., Ed.; N.B.S. Special Publication 314: Washington D.C., 1969; Chapter 4, p 136.

(21) Bates, R. G. *Determination of pH - Theory and Practice*, 2nd ed.; Wiley: New York, 1973; p 379.

(22) Mussini, T. Concentrated “equitransferent” salt bridges to minimize the liquid junction potentials? A revision. *J. Chem. Educ.* **1988**, *65*, 242–243.

(23) Reference , pp 182−185, 225−228.

(24) King, E. J. In *Physical Chemistry of Organic Solvent Systems*; Covington, A. K., Dickinson, T., Eds.; Plenum Press: London, 1973; Chapter 3, p 338.

(25) Rondinini, S.; Mussini, P. R.; Mussini, T. Autoprotolysis constants in nonaqueous solvents and aqueous organic solvent mixtures. *Pure Appl. Chem.* **1987**, *59*, 1693–1702.

(26) Izutsu, K. *Electrochemistry in Nonaqueous Solutions*; Wiley VCH Verlag: Weinheim, Germany, 2002; p 43−78,. 182.

(27) Owen, B. B. Direct measurement of the primary, secondary and total medium effects of acetic acid. *J. Am. Chem. Soc.* **1932**, *54*, 1758–1769.

(28) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd ed.; Butterworths: London, 1965; pp 352−355, 364−369.

(29) Woolley, E. M.; Tomkins, J.; Hepler, L. G. Ionization constants for very weak organic acids in aqueous solution and apparent ionization constants for water in aqueous organic mixtures. *J. Solution Chem.* **1972**, *1*, 341–351.

(30) Roses, M.; Rafols, C.; Bosch, E. Autoprotolysis in aqueous organic solvent mixtures. *Anal. Chem.* **1993**, *65*, 2294–2299.

(31) Marcus, Y. *Solvent mixtures. Properties and selective solvation*; Marcel Dekker: New York, 2002; pp 95−97.

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