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

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Following the IUPAC criteria, four primary standards (pH_{PS}) and three secondary standards (pH_{SS}) have been determined at various temperatures using Harned's reversible cell and Baucke's nonreversible cell, respectively, the solvent media Z studied being *N*-methylacetamide and its mixture with water at 0.50 mass fraction. Their internal consistency was ascertained by the linear pH dependence of the emf of the cell (Pt|H_2|pH standards in Z||NH_4Cl bridge in Z|AgCl|Ag|Pt). Essential thermodynamic functions (standard emfs $E°$ of cell and ionization constants of orthophthalic acid) hitherto unknown in the pertinent solvent Z had also to be determined from the emfs of the appropriate reversible cells. These pH_{PS} and pH_{SS} acquisitions enable the user to perform routine pH_X measurements by the regular operational cell. A supplementary systematic search has been performed according to the method of Helmholtz transference cells both in *N*-methylacetamide and in its $w = 0.50$ mixture with water, to single out appropriately equitransferent salt bridges for the abatement of liquid junction potentials in the operational pH cells. The intercomparability of the pH scales in the above solvents Z with that in pure water is discussed in terms of the solvent autoprotolysis constants in conjunction with the primary medium effects upon the H^+ ion.

Introduction

The present study is part of a standing program on the standardization of pH measurements in nonaqueous and aqueous−organic solvents, which this Research Group started in accord with the Electroanalytical Chemistry Commission of IUPAC.[1] Recently, the IUPAC issued a key innovatory document (Recommendations 2002) that reassesses the basic rationale, the methodology of establishing the pertinent reference solutions (pH standards), and the procedure for the evaluation of the uncertainty budget of the latter.[2] 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 neat water only, because water is the solvent medium hitherto studied much more extensively. The situation is, however, very different in the field of nonaqueous or mixed solvents, which embraces a practically unlimited number of solvent systems. In fact, regrettably, only for 10 binary solvent systems (i.e., of the aqueous + organic cosolvent type),[1,3−7] besides neat formamide,[8] were the required primary and/or secondary standards determined hitherto.

The *N*-methylacetamide ($\epsilon = 178$ at 303 K) chosen for the present work is among the most superpermittive protic media ever explored: it is characterized by good solubilizing and ionizing properties and would prospectively be an interesting medium for designs of innovative nonaqueous cells. Its 0.50 mass fraction in admixture with water has also been included in this study for completeness, to verify the behavior of several standard pH buffers in aqueous−organic media.

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Procedure for the Determination of pH Standards

The IUPAC procedure[2] prescribes that the primary standard, pH_{PS}, be determined exclusively by the "primary method" based on measuring the electromotive force (emf) E_A of Harned's reversible cell

$$\mathrm{Pt}|\mathrm{H_2}\ (101.325\ \mathrm{kPa})|\text{primary standard buffer}\ (m_{PS}) + \mathrm{KCl}\ (m_{Cl})\ \text{in Z}|\mathrm{AgCl}|\mathrm{Ag}|\mathrm{Pt} \quad \text{(A)}$$

which obeys the Nernstian equation

$$(E_A - E°)/k = \log(m_H\gamma_H/m°) + \log(m_{Cl}\gamma_{Cl}/m°) = -\mathrm{pH} + \log(m_{Cl}/m°) + \log(\gamma_{Cl}) \quad (1)$$

where $E°$ is the standard emf of the cell, γ represents the activity coefficient 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 1 are known or determinable in strict thermodynamic terms, except the extra-thermodynamic quantity $\log(\gamma_{Cl})$, which is to be computed by the IUPAC-endorsed Bates−Guggenheim convention in the form[1,3]

$$\log(\gamma_{Cl}) = -A_Z I^{1/2}/(1 + 1.5\,[\epsilon_W\rho_Z/\epsilon_Z\rho_W]^{1/2} I^{1/2}) = -A_Z I^{1/2}/(1 + \beta\, I^{1/2}) \quad (2)$$

where A_Z is the classical Debye−Hückel constant appropriate to the solvent Z, I is the ionic strength of the cell electrolyte, ϵ and ρ are, respectively, relative permittivities and densities of the components marked by subscripts, and β is henceforth used as an abbreviation for the quantity $1.5[\epsilon_W\rho_Z/\epsilon_Z\rho_W]^{1/2}$.

Accurate values of the standard emfs $E°$ required by eq 1 are available from the literature[9] for *N*-methylacetamide, but

10.1021/je600581j CCC: $37.00
Published on Web 08/07/2007

not for the $w_{NMA} = 0.5$ mass fraction of *N*-methylacetamide in admixture with water; therefore, a supplementary separate determination of $E°$ at various temperatures had to be necessarily included in the present work. This was performed according to the classical method based on measurements of the emf E_B of the cell

$$\mathrm{Pt|H_2\ (101.325\ kPa)|HCl}\ (m)\ \mathrm{in\ Z|AgCl|Ag|Pt} \qquad \mathrm{(B)}$$

having a pertinent Nernstian equation of

$$E_B = E° - 2k \log(m\gamma_{\pm})_{HCl} \qquad (3)$$

In the subsequent calculations, Hitchcock's equation[10,11] for the mean molal activity coefficients $\gamma_{\pm}$ has here proved to produce the best fit; thus, combining it with eq 3 and rearranging, the following function Φ linear in m can be defined:

$$\Phi = E_B + 2k \log(m/m°) - 2k\, A_Z\sqrt{m} - \log(1 + 2M_Z m) = E° - kbm \quad (4)$$

The intercept at $m = 0$ of the Φ versus m straight line yields the sought $E°$ value.

The obtainment of the pertinent $E°$ data is not the only supplementary experimentation to be performed as a prerequisite to the E_A data processing following eq 1. In fact, obtaining pH data from the combined eqs 1 and 2 requires quantification of the ionic strength I, which, in the case of the potassium hydrogen orthophthalate buffer (KHPh), may to some extent depend on the value of the first ionization constant K_1 of the orthophthalic acid (H_2Ph) in each solvent Z studied, the pK_1 value of which may be expected to be ≈ 3. The pK_1 determination has here been performed by measuring the emf E_C of the reversible Harned and Ehlers'[12] cell C:

$$\mathrm{Pt|H_2\ (101.325\ kPa)|\ H_2Ph}\ (m) + \mathrm{KHPh}\ (m_1) + \mathrm{KCl}\ (m_2)\ \mathrm{in\ Z|AgCl|Ag|Pt} \quad \mathrm{(C)}$$

The extrapolation function Φ' for E_C is of the form

$$\Phi' = E_C - E° + k \log(mm_2/m_1) = k(\mathrm{p}K_1) - k(b_{Cl^-} - b_{HPh^-})\, I \quad (5)$$

The steps of the E_C data processing are described in detail in a recent paper[6] and thus need not be repeated here.

According to the cited IUPAC document,[2] the secondary standards, pH_{SS}, could be determined by either of the nonreversible cells D or E, for which the diagrams are described below:

$$\mathrm{Pt|H_2\ (101.325\ kPa)|primary\ standard\ buffer}\ (m_{PS})\ \mathrm{in\ Z\ |salt\ bridge\ in\ Z|}$$

$$\mathrm{secondary\ standard\ buffer}\ (m_{SS})\ \mathrm{in\ Z|H_2\ (101.325\ kPa)|Pt} \quad \mathrm{(D)}$$

$$\mathrm{Pt|H^+\text{-sensing glass electrode|secondary standard buffer}}\ (m_{SS}) + \mathrm{KCl}\ (m_{Cl})\ \mathrm{in\ Z|AgCl|Ag|Pt} \quad \mathrm{(E)}$$

Cell D, where the secondary standard pH_{SS} is compared with a selected primary standard pH_{PS}, can be used in two alternative configurations: (i) with the primary and the secondary buffer having the same nominal composition ($m_{PS} = m_{SS}$), thus resulting in a symmetrical cell; or (ii) with $m_{PS} \neq m_{SS}$, namely, an unsymmetrical cell. Scheme ii is the one used here. From the emf E_D of cell D the relevant expression for the secondary standard pH_{SS} is

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

where the residual liquid junction potential E_{JR} can be taken as zero only if the salt bridge in Z is chosen critically. To this purpose, another, integrative search is essential to single out one or more alkali chlorides MCl characterized by an appropriate level of equitransference, that is, by ionic transference numbers satisfying the condition $t_+ = t_- = 0.5$ as closely as possible. Therefore, a systematic investigation has here been carried out by the transference cell method, which was recently reassessed critically by our research group.[13,14] This experimentation hinges on emf E_F measurements on the transference cell (F)

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

where m_2 (variable) > m_1 (fixed), in combination with the parallel potential difference E_G of the nontransferent double cell (G)

$$\mathrm{Ag|AgCl|MCl}\ (m_2)|\text{M-amalgam—M-amalgam}\ |\mathrm{MCl}\ (m_1)\mathrm{AgCl|Ag} \quad \mathrm{(G)}$$

with $E_F \leq E_G$. In fact, for the pertinent transference number t_{M+} the following thermodynamic equation holds

$$t_{M^+} = dE_F/dE_G \qquad (7)$$

in combination with the interrelated eqs 8 and 9

$$t_{M^+} + t_{Cl^-} = 1 = dE_F/dE_G + dE_H/dE_G \qquad (8)$$

$$E_F + E_H = E_G \quad \text{and} \quad dE_F + dE_H = dE_G \qquad (9)$$

where E_H is the emf of the transference cell H:

$$\text{M-amalgam}|\mathrm{MCl}\ (m_1)||\mathrm{MCl}\ (m_2)|\text{M-amalgam} \qquad \mathrm{(H)}$$

The application of this set of equations was described in detail earlier.[8,13,14]

Another important aspect is the verification of the internal consistency of the primary pH_{PS} and/or secondary (pH_{SS}) standards thus found. This can be accomplished by measuring the potential emf E_I of cell I

$$\mathrm{Pt|H_2\ (101.325\ kPa)|pH_{PS}\ and/or\ pH_{SS}\ solution\ |salt\ bridge|reference\ electrode} \quad \mathrm{(I)}$$

where the whole sequence of the standards in question is to be tested, and it rests on the following rationale: if the standards determined above had exact mutual consistency (ideal conditions, with perfect salt bridge), then plotting E_I versus pH_{PS} (and/or pH_{SS}) should produce a straight line of theoretical Nernstian slope factor $k = (\ln 10)RT/F$. Clearly, under real conditions of experimental error the practical slope factor k' could somewhat differ from the theoretical one. However, as shown later, the k' values observed in the present work are in good accord with the theoretical value k, thus denoting an excellent degree of mutual consistency among the above standards.

Experimental Section

The hydrogen electrodes in cells A, B, C, D, and I were prepared as in our previous works in aqueous–organic media.[6,7] The silver/silver halide electrodes in cells A, B, C, D, and F were prepared according to the bielectrolytic method.[15,16] The solutions were prepared by mass from the following chemicals: potassium hydrogen phthalate (Aldrich, 99.99 %), diso-

Table 1. Averaged Electromotive Forces E_A of Harned's Cell A Measured in Quadruplicate, the Solvent Z Being the Neat Amide or the Amide + Water Mixture at Mass Fraction $w = 0.5$, as a Function of Molality m_{Cl} of KCl, at Various Temperatures T, To Obtain the Corresponding Primary Standards pH_{PS} for the Potassium Hydrogen Orthophthalate Buffer (KHPh)[a]

	E_A/V							
N-methylacetamide					*N*-methylacetamide, $w = 0.5$			
m_{Cl}/(mmol·kg^{-1})	$T = 308.15$ K	$T = 313.15$ K	$T = 318.15$ K	$T = 323.15$ K	m_{Cl}/(mmol·kg^{-1})	$T = 298.15$ K	$T = 308.15$ K	$T = 318.15$K
2.014	0.67111	0.67170	0.66289	0.66568	20.210	0.61654	0.62450	0.62608
3.009	0.66089	0.65341	0.65591	0.66119	35.363	0.60016	0.60481	0.60701
3.507	0.66292	0.66590	0.65909	0.66312	50.602	0.59128	0.59795	0.60053
4.011	0.66877	0.66222	0.66550	0.66442	70.704	0.58118	0.58372	0.58614
4.994	0.66084	0.67103	0.65480	0.66108	85.810	0.57634	0.57913	0.58141
5.509	0.65786	0.67768	0.66211	0.66657	101.178	0.57088	0.57354	0.57584
$E°$/V	0.21187	0.20573	0.20091	0.19456		0.25804	0.25058	0.24270
A_Z/(kg$^{1/2}$·mol$^{-1/2}$)	0.1452	0.1501	0.1558	0.1623		0.4228	0.4358	0.4520
ϵ_Z	172.2	165.5	158.7	151.8		89.0	84.2	79.4
ρ_Z/(kg·dm^{-3})	0.9461	0.9420	0.9378	0.9336		1.0027	0.9958	0.9889
β/(kg$^{1/2}$·mol$^{-1/2}$)	0.9646	0.9717	0.9799	0.9895		1.411	1.415	1.423

[a] Also quoted (see text for sources): standard emfs $E°$ and Debye−Hückel constant A_Z, together with the pertinent permittivities ϵ and densities ρ of the solvent studied, and the quantity β of eq 2.

Table 2. Averaged Electromotive Forces E_A of Harned's Cell A Measured in Quadruplicate, in Mass Fraction $w = 0.5$ of *N*-Methylacetamide in Admixtures with Water, as a Function of Molality m_{Cl} of KCl, at Various Temperatures T, To Obtain the Corresponding Primary Standards pH_{PS} for the Buffers Indicated[a]

	E_A/V						
N-methylacetamide, $w = 0.5$; equimolal phosphate buffer				*N*-methylacetamide, $w = 0.5$; carbonate buffer			
m_{Cl}/(mmol·kg^{-1})	$T = 298.15$ K	$T = 308.15$ K	$T = 318.15$ K	m_{Cl}/(mmol·kg^{-1})	$T = 298.15$ K	$T = 308.15$ K	$T = 318.15$ K
5.038	0.83484	0.84302	0.85011	5.027	1.02983	1.04012	1.05085
12.506	0.80711	0.81837	0.82226	20.030	0.99132	1.00063	1.01024
19.972	0.79598	0.80369	0.81040	35.156	0.97584	0.98551	0.99419
30.000	0.78117	0.78844	0.79470	50.216	0.96585	0.97499	0.98305
39.989	0.76892	0.77639	0.78269	70.215	0.95586	0.96416	0.97219
50.002	0.76345	0.77111	0.77700	85.328	0.95415	0.96221	0.97013

[a] The data of $E°$, Debye−Hückel constant A_Z, the pertinent permittivities ϵ and densities ρ, and the quantity β of eq 2 are the same as in Table 1.

dium hydrogen phosphate and potassium dihydrogen phosphate (Carlo Erba, >99.5 %), sodium hydrogen carbonate and sodium carbonate (Fluka, >99.5 %), potassium hydrogen tartrate (Aldrich, 99 %), potassium tetraoxalate (Fluka, >99.5 %), and *N*-methylacetamide (Aldrich, ≥99 %). The measurements of cell electromotive forces (emf) were performed by a model 619 Keithley differential electrometer of input impedance higher than 10^{14} Ω. The precision of the emf measurements was ±0.01 mV. All emfs of the cells A, B, and C were measured in quadruplicate, and the values quoted in the pertinent tables are average values. The thermostatic apparatus was described earlier,[16] and it ensured a temperature control of ±0.02 K in the cell.

Results and Discussion

Table 1 reports the values of the emfs E_A of Harned's cell A measured for the primary standard buffer 0.05 *m* potassium hydrogen orthophthalate [the "phthalate" buffer, KHPh], containing various molalities m_{Cl} of added KCl, in neat *N*-methylacetamide (melting point, 303 K) within the temperature range from (308.15 to 323.15) K as well as in *N*-methylacetamide in admixture with water at mass fraction 0.5, within the temperature range from (298.15 to 318.15) K. Accurate values for such ancillary quantities as the relative permittivities ϵ and densities ρ required by the present computations are available from the work of Dawson et al.[17] for neat *N*-methylacetamide and from Casteel and Amis[18] for the *N*-methylacetamide + water mixture. The parallel ϵ_W and ρ_W data for pure water medium, which are required by eq 2, have been taken from Robinson and Stokes' tabulation.[19] For the required $E°$ values, see later on. Table 2 quotes the E_A values for the other primary standards studied (the "carbonate" and the "equimolal phosphate" buffers) in the 0.5 mass fraction of *N*-methylacetamide. The pH values calculated therefrom show slight differences due to ionic interactions between KCl and the relevant buffer, and this effect is removed by plotting these pH values against the corresponding m_{Cl} values: the pH value extrapolated to $m_{Cl} = 0$ is finally assigned the qualification of primary standard pH_{PS}, as shown in Figure 1. The pH_{PS} values for the above primary buffers obtained at each temperature and solvent composition are found in Table 3 together with the pertinent expanded uncertainties U.[2] These quoted U values should be further added by 0.01 (accounting for the uncertainty contributed by the Bates−Guggenheim convention[2,3]) to make pH_{PS} traceable to SI, as from the IUPAC protocol.[2] For the $E°$ values required by the key eq 1 for the pH calculation in neat *N*-methylacetamide have been used the accurate values obtained by Dawson et al.[9] in their key thermodynamic study of cell B in duplicate or triplicate series over extended ranges of temperature and HCl molalities. However, the parallel $E°$ values in the 0.5 mass fraction of *N*-methylacetamide in water were hitherto missing. Therefore, this lack has been eliminated using the procedure based on the classical cell B: the measured emf E_B values of the latter are processed in terms of the linear function Φ defined by eq 4. the intercept of Φ at $m = 0$ gives $E°$. The measured E_B values are quoted in Table 4 together with the resulting $E°$ values and the pertinent standard errors. Once the required $E°$ value is attained, the mean ionic activity coefficients $\gamma_\pm$ of HCl in the present (NMA + W) solvent mixture within the HCl molality explored at each temperature can be obtained using eqs 3 and 4. These values are shown in Figure 2. It turns out that the $\gamma_\pm$

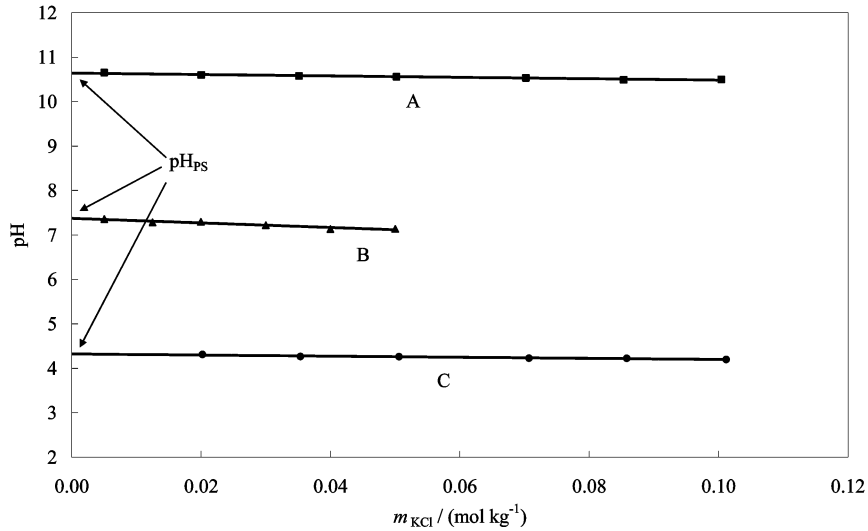

Figure 1. Extrapolation to $m_{KCl} = 0$ of the pH values calculated through eqs 1 and 2 to obtain the corresponding primary standards pH$_{PS}$ at each temperature, in the pertinent solvents: A, carbonate; B, equimolal phosphate; C, phthalate buffers, in NMA + water $w = 0.5$.

Table 3. pH Standards for Different Buffers in Various Solvents at Various Temperatures *T*, with Corresponding Expanded Uncertainties U^2 (See Text)

buffer	standard		*T*/K
	Solvent: *N*-Methylacetamide		
phthalate[a]	primary	4.65 ± 0.10	308.15
		4.32 ± 0.16	313.15
		4.38 ± 0.10	318.15
		4.39 ± 0.04	323.15
	Solvent: *N*-Methylacetamide + Water, $w = 0.5$		
phthalate[a]	primary	4.323 ± 0.011	298.15
		4.382 ± 0.029	308.15
		4.339 ± 0.027	318.15
equimolal phosphate[b]	primary	7.372 ± 0.022	298.15
		7.331 ± 0.020	308.15
		7.244 ± 0.019	318.15
carbonate[c]	primary	10.642 ± 0.011	298.15
		10.515 ± 0.010	308.15
		10.399 ± 0.011	318.15
tetraoxalate[d]	secondary	1.78 ± 0.16	298.15
		1.85 ± 0.19	308.15
		1.85 ± 0.09	318.15
tartrate[e]	secondary	4.00 ± 0.16	298.15
		4.08 ± 0.12	308.15
		4.03 ± 0.09	318.15
unequimolal phosphate[f]	secondary	7.96 ± 0.16	298.15
		7.95 ± 0.12	308.15
		7.87 ± 0.09	318.15

[a] 0.05 *m* potassium hydrogen orthophthalate. [b] 0.025 *m* Na_2HPO_4 + 0.025 *m* KH_2PO_4. [c] 0.025 *m* Na_2CO_3 + 0.025 *m* $NaHCO_3$. [d] 0.05 *m* tetraoxalate [$KH_3(C_2O_4)_2 \cdot 2H_2O$]. [e] Saturated potassium hydrogen tartrate [$KHC_4H_4O_6$]. [f] 0.03043 *m* Na_2HPO_4 + 0.008695 *m* KH_2PO_4.

values in (NMA + W) are markedly higher than those in water,[20] as expected from the higher permittivity of (NMA + W) with respect to that in water. In the case of the KHPh buffer the quantification of the ionic strength *I* appearing in eq 2 requires the further knowledge of the first ionization constant K_1 of the orthophthalic H_2Ph, that is, the parent acid to KHPh. As described in a recent paper[6] the relevant pK_1 values can be obtained by elaborating on the emf values E_C of Harned and Ehlers' cell C, which again requires the knowledge of the $E°$ values mentioned above, through an iterative calculation procedure.[6] The measured E_C values together with the resulting pK_1 values in *N*-methylacetamide and in its 0.5 mass fraction in water are quoted in Table 5.

The emf E_D values of cell D for the determination of the secondary standards pH$_{SS}$ are quoted in Table 6. To this purpose,

Table 4. Averaged Potential Differences E_B of Cell B, Measured in Quadruplicate, in Mass Fraction $w = 0.50$ of *N*-Methylacetamide in Admixture with Water, as a Function of Molality *m* of HCl, at Various Temperatures *T*, To Obtain the Pertinent Standard Values $E°$[a]

	E_B/V *N*-methylacetamide, $w = 0.5$		
m/(mmol·kg^{-1})	$T = 298.15$ K	$T = 308.15$ K	$T = 318.15$ K
5.059	0.53332	0.53461	0.53624
7.075	0.51577	0.51761	0.51861
29.817	0.44470	0.44388	0.44283
50.118	0.41904	0.41754	0.41468
70.357	0.40155	0.39924	0.39700
85.083	0.39214	0.38932	0.38707
100.116	0.38445	0.38196	0.37887
$E°$/V	0.25804 ± 0.00026	0.25058 ± 0.00032	0.24270 ± 0.00028
ϵ_Z	89.0	84.2	79.4
ρ_Z/(kg·dm^{-3})	1.0027	0.9958	0.9889
A_Z/(kg$^{1/2}$·mol$^{-1/2}$)	0.4228	0.4358	0.4520
b/(kg·mol^{-1})	0.7115	0.7346	0.7531

[a] The required ancillary data of ϵ, ρ, and Debye−Hückel constants A_Z are also quoted, together with the parameter *b* of eq 4.

the tetraoxalate, the tartrate, and the unequimolal phosphate buffers were studied versus the three primary standards pH$_{PS}$ offered by the phthalate, the equimolal phosphate, and the carbonate buffers, used widely as fixed references in cell D at each temperature, employing the saturated solution of NH_4Cl as the most appropriate salt bridge hitherto characterized in the (*N*-methylacetamide + water) solvent mixtures explored. Thus, for each of the three above secondary buffers (obviously at each temperature) the pertinent pH$_{SS}$ value has been determined versus each of the three primary buffers of known pH$_{PS}$. For the three pH$_{SS}$ values thus computed by eq 6, the weighted mean has been quoted in Table 3 together with the pertinent uncertainty figures, for a total of 27 cases.

Once the above three primary standards pH$_{PS}$ and the three secondary standards pH$_{SS}$ in (*N*-methylacetamide + water) have been acquired, the verification of their internal consistency is to be performed through the emf E_I of cell I, the values for which are quoted in Table 7. In cell I the reference electrode was a calomel electrode having a built-in NH_4Cl salt bridge. The slopes k' of the E_I versus pH$_{PS}$ straight lines are in good agreement with the theoretical value $k = (\ln 10)RT/F$ at each temperature of experiment. The very small $(k' - k)$ deviations observed are ascribed to overlapping of pH-dependent residual liquid junction potentials.[21]

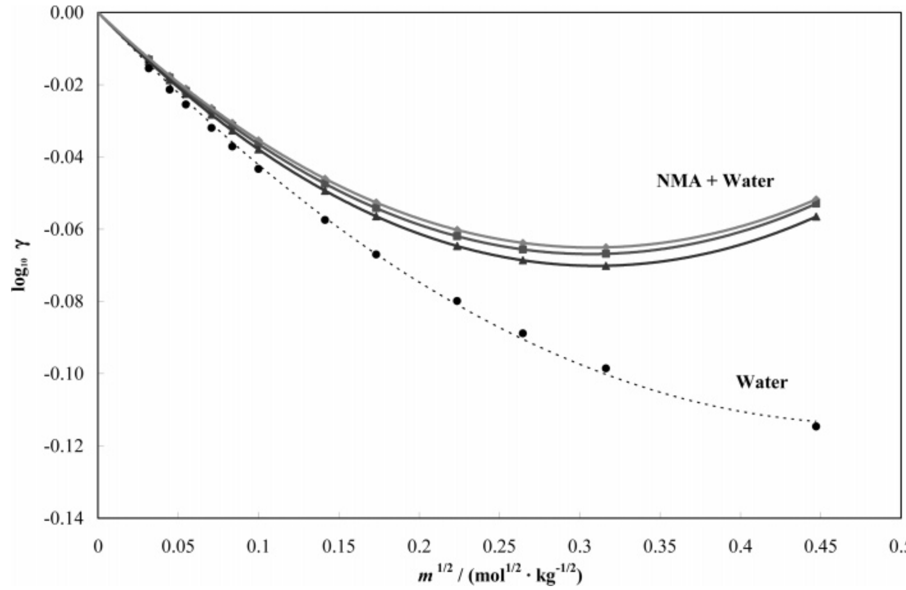

Figure 2. Debye−Hückel plot of log $\gamma_{\pm}$ versus $m^{1/2}$ for HCl in solvent Z (=50 mass % *N*-methylacetamide + water) at different temperatures: ◆, 298.15 K; ■, 308.15 K; ▲, 318.15 K. For comparison, from the literature[33] the corresponding plot pertaining to pure water solvent at 298.15 K is quoted, ●.

Table 5. Averaged Potential Differences E_C of Harned and Ehlers' Cell C, Measured in Quadruplicate, in Neat *N*-Methylacetamide and in Mass Fraction $w = 0.5$ of *N*-Methylacetamide in Admixture with Water, as a Function of Molality *m* of Orthophthalic Acid H_2Ph, at Various Temperatures *T*, To Obtain the Corresponding Constants pK_1[a]

E_C/V						
N-methylacetamide			*N*-methylacetamide, $w = 0.5$			
m/(mmol·kg^{-1})	T = 308.15 K	T = 323.15 K	m/(mmol·kg^{-1})	T = 298.15 K	T = 308.15 K	T = 318.15 K
1.00	0.63846	0.64849	5.00	0.57105	0.57375	0.57581
1.49	0.62484	0.62416	8.00	0.55867	0.55945	0.56149
2.70	0.60549	0.60407	12.00	0.54683	0.54775	0.54787
2.99	0.60147	0.60075	15.00	0.54330	0.54314	0.54278
pK_1	3.918	4.037		2.707	2.705	2.715
SD	±0.012	±0.012		±0.032	±0.012	±0.027

[a] The required ancillary data of $E°$, ϵ, ρ, and Debye−Hückel constants A_Z are the same as in Table 1.

Table 6. Averaged Potential Differences E_D of Cell D for Three Secondary Standard Buffers Measured in Duplicate against Three Primary Standard Buffers at Different Temperatures *T* in Mass Fractions $w = 0.5$ of *N*-Methylacetamide

		E_D/V primary buffer		
secondary buffer	T/K	phthalate	equimolal phosphate[a]	carbonate
tetraoxalate	298.15	0.15244	0.30340	0.53770
	308.15	0.15532	0.31076	0.54590
	318.15	0.15760	0.32005	0.55541
tartrate	298.15	0.02123	0.17219	0.40649
	308.15	0.01945	0.17489	0.41004
	318.15	0.01992	0.18238	0.41774
unequimolal phosphate[b]	298.15	−0.21304	−0.06208	0.17222
	308.15	−0.21741	−0.06197	0.17318
	318.15	−0.22244	−0.05998	0.17538

[a] 0.025 m Na_2HPO_4 + 0.025 m KH_2PO_4. [b] 0.03043 m Na_2HPO_4 + 0.008695 m KH_2PO_4.

Intercomparing pH Scales in Different Solvents. The primary and secondary standards determined in each solvent according to the IUPAC-endorsed procedure are physically comparable neither among themselves nor with aqueous standards. As explained by Bates[22] and in IUPAC documents,[1,3] this intercomparability problem involves the simultaneous discussion of the nominal range of the pH scale (defined as pK_{AP}, where K_{AP} is the autoprotolysis constant of the solvent Z considered) and of the primary medium effect[23] on the H^+ ion (which is the standard Gibbs energy change $[\Delta G°_{W\to Z}]_{H+}$ accompanying the transfer of H^+ from the standard state in water to the standard state in the solvent Z). $[\Delta G°_{W\to Z}]_{H+}$ implies a correction $\Delta pH = -[\Delta G°_{W\to Z}]_{H+}/(2.303RT)$ to any pH standard and any unknown pH_X measured in the solvent Z to make them comparable with aqueous pH values. In the cases of amides and monoalkyl-substituted amides, $[\Delta G°_{W\to Z}]_{H+}$ is negative (i.e., the process H^+[W,standard state] → H^+[Z,standard state] is spontaneous); therefore, the above ΔpH correction is *positive*; that is, the pertinent scales of pH are shifted to the positive direction with respect to the aqueous scale taken as ultimate reference.

Table 7. Potential Differences E_I of the Cell I on Six (Primary and Secondary) pH Standards at Various Temperatures *T*, in *N*-Methylacetamide at Mole Fraction $w = 0.5$ in Admixture with Water

		E_I/V		
standard	buffer	T = 298.15 K	T = 308.15 K	T = 318.15 K
pH_{PS}	carbonate	0.91681	0.92342	0.93244
pH_{SS}	unequimolal phosphate[a]	0.74459	0.75025	0.75706
pH_{PS}	equimolal phosphate[b]	0.68251	0.68828	0.69708
pH_{PS}	phthalate	0.53155	0.53284	0.53462
pH_{SS}	tartrate	0.51032	0.51339	0.51470
pH_{SS}	tetraoxalate	0.37911	0.37752	0.37703

[a] 0.03043 m Na_2HPO_4 + 0.008695 m KH_2PO_4. [b] 0.025 m Na_2HPO_4 + 0.025 m KH_2PO_4.

Indeed, pK_{AP} can be determined by a thermodynamic method based on reversible cells, but so far the available pK_{AP} data are

Table 8. Electromotive Forces E_F and E_G of the Cells F and G, Respectively, for the Singling out and Characterization of New Salt Bridges in NMA and NMA + W (w = 0.5)[a]

Solvent: *N*-Methylacetamide								
LiCl (m_1 = 0.010015 mol·kg^{-1} and γ_1 = 0.969); a_0 = 0.43 nm; $t°_{Li^+}$ = (0.403 ± 0.008)								
$1000m_2$/(mol·kg^{-1})	2.012	2.956	4.961	7.073	10.015	15.057	20.084	24.965
E_F/V	−0.03466	−0.02495	−0.01491	−0.00949	0	0.00717	0.01423	0.01831
E_G/V	−0.08294	−0.06301	−0.03622	−0.01792	0	0.02094	0.03569	0.04680
γ_2	0.985	0.982	0.978	0.973	0.969	0.962	0.956	0.952
NaCl (m_1 = 0.009999 mol·kg^{-1} and γ_1 = 0.968); a_0 = 0.40 nm; $t°_{Na^+}$ = (0.406 ± 0.017)								
$1000m_2$/(mol·kg^{-1})	2.030	2.937	7.048	9.999	15.008	20.000		
E_F/V	−0.03335	−0.02232	−0.00840	0	0.01007	0.01618		
E_G/V	−0.08238	−0.06325	−0.01801	0	0.02085	0.03555		
γ_2	0.985	0.982	0.973	0.968	0.962	0.956		
KCl (m_1 = 0.004000 mol·kg^{-1} and γ_1 = 0.980); a_0 = 0.38 nm; $t°_{K^+}$ = (0.450 ± 0.005)								
$1000m_2$/(mol·kg^{-1})	0.469	1.040	2.012	3.050	5.096	4.000		
E_F/V	−0.05031	−0.03027	−0.01582	−0.00582	0.00572	0		
E_G/V	−0.11124	−0.06989	−0.03561	−0.01404	0.01251	0		
γ_2	0.993	0.989	0.985	0.982	0.977	0.980		
NH_4Cl (m_1 = 0.009985 mol·kg^{-1} and γ_1 = 0.981); a_0 = 0.39 nm; $t°_{NH_4^+}$ = (0.476 ± 0.014)								
$1000m_2$/(mol·kg^{-1})	2.010	5.035	7.053	9.985	15.004	20.003	24.973	
E_F/V	−0.04295	−0.01955	−0.01240	0	0.00766	0.01470	0.01833	
E_G/V	−0.08331	−0.03557	−0.01805	0	0.02113	0.03605	0.04755	
γ_2	0.989	0.985	0.983	0.981	0.978	0.976	0.974	
RbCl (m_1 = 0.004003 mol·kg^{-1} and γ_1 = 0.980); a_0 = 0.36 nm; $t°_{Rb^+}$ = (0.398 ± 0.014)								
$1000m_2$/(mol·kg^{-1})	0.517	2.003	3.038	4.003				
E_F/V	−0.04206	−0.01556	−0.00482	0				
E_G/V	−0.10627	−0.03586	−0.01426	0				
γ_2	0.993	0.985	0.982	0.980				
CsCl (m_1 = 0.004429 mol·kg^{-1} and γ_1 = 0.978); a_0 = 0.30 nm; $t°_{Cs^+}$ = (0.446 ± 0.009)								
$1000m_2$/(mol·kg^{-1})	0.568	1.140	2.158	3.341	5.470	4.429		
E_F/V	−0.04873	−0.03144	−0.01844	−0.00691	0.00327	0		
E_G/V	−0.10660	−0.07035	−0.03724	−0.01458	0.01090	0		
γ_2	0.992	0.989	0.985	0.981	0.976	0.978		
Solvent: *N*-Methylacetamide + Water, w = 0.5								
LiCl (m_1 = 0.010056 mol·kg^{-1} and γ_1 = 0.918); a_0 = 0.43 nm; $t°_{Li^+}$ = (0.394 ± 0.009)								
$1000m_2$/(mol·kg^{-1})	2.107	3.113	4.997	7.169	10.056	14.963	19.976	25.192
E_F/V	−0.03116	−0.02569	−0.01382	−0.00716	0	0.00591	0.01281	0.01629
E_G/V	−0.07806	−0.05844	−0.03475	−0.01677	0	0.01958	0.03374	0.04505
γ_2	0.959	0.951	0.940	0.930	0.918	0.904	0.892	0.881
NaCl (m_1 = 0.009987 mol·kg^{-1} and γ_1 = 0.918); a_0 = 0.40 nm; $t°_{Na^+}$ = (0.475 ± 0.002)								
$1000m_2$/(mol·kg^{-1})	2.076	3.033	5.041	7.049	9.987	14.933	19.991	25.021
E_F/V	−0.03725	−0.02845	−0.01609	−0.00895	0	0.00922	0.01597	0.02132
E_G/V	−0.07846	−0.05938	−0.03396	−0.01726	0	0.01982	0.03409	0.04502
γ_2	0.960	0.952	0.939	0.930	0.918	0.903	0.890	0.880
KCl (m_1 = 0.010002 mol·kg^{-1} and γ_1 = 0.918); a_0 = 0.38 nm; $t°_{K^+}$ = (0.484 ± 0.016)								
$1000m_2$/(mol·kg^{-1})	2.055	3.022	5.007	6.974	10.002	14.968	19.959	24.978
E_F/V	−0.04068	−0.03205	−0.01898	−0.00918	0	0.01007	0.01344	0.01716
E_G/V	−0.07902	−0.05962	−0.03435	−0.01786	0	0.01984	0.03392	0.04484
γ_2	0.960	0.952	0.939	0.930	0.918	0.902	0.890	0.879
NH_4Cl (m_1 = 0.010013 mol·kg^{-1} and γ_1 = 0.918); a_0 = 0.39 nm; $t°_{NH_4^+}$ = (0.515 ± 0.003)								
$1000m_2$/(mol·kg^{-1})	2.069	3.039	5.085	7.004	10.013	15.025	20.050	25.060
E_F/V	−0.04016	−0.02974	−0.01702	−0.00921	0	0.01072	0.01841	0.02348
E_G/V	−0.07874	−0.05940	−0.03364	−0.01770	0	0.01998	0.03410	0.04495
γ_2	0.960	0.952	0.939	0.930	0.918	0.902	0.890	0.880
RbCl (m_1 = 0.009997 mol·kg^{-1} and γ_1 = 0.917); a_0 = 0.36 nm; $t°_{Rb^+}$ = (0.516 ± 0.004)								
$1000m_2$/(mol·kg^{-1})	2.007	3.021	4.981	7.020	9.997	14.964	19.986	24.975
E_F/V	−0.04142	−0.03124	−0.01858	−0.01016	0	0.00919	0.01689	0.02327
E_G/V	−0.08017	−0.05960	−0.03457	−0.01750	0	0.01985	0.03399	0.04482
γ_2	0.960	0.952	0.939	0.929	0.917	0.902	0.889	0.878
CsCl (m_1 = 0.009997 mol·kg^{-1} and γ_1 = 0.916); a_0 = 0.30 nm; $t°_{Cs^+}$ = (0.530 ± 0.002)								
$1000m_2$/(mol·kg^{-1})	1.979	3.016	4.996	6.983	9.997	14.976	19.989	25.011
E_F/V	−0.04307	−0.03159	−0.01825	−0.00970	0	0.01004	0.01773	0.02383
E_G/V	−0.08080	−0.05963	−0.03440	−0.01774	0	0.01985	0.03393	0.04480
γ_2	0.960	0.951	0.938	0.928	0.916	0.900	0.887	0.875

[a] γ_1 and γ_2 = mean ionic activity coefficients of MCl at molality m_1 (fixed) and m_2.

scarce;[24,25] yet $[\Delta G°_{W\rightarrow Z}]_{H+}$, a quantity concerning the single H^+, falls outside the domain of exact thermodynamics[22,26] and thus requires extra-thermodynamic methods or assumptions, and the relevant data are even scarcer.[22,27] For the present case, pK_{AP} data are available from the work by Asuero et al.,[28] which leads to 14.79 for pure *N*-methylformamide and 16.74 for its 0.5 mass fraction in water, not much different from the aqueous values. For the corresponding primary medium effects on H^+, in terms of the ΔpH corrections, we have +2.3 and +1.2, respectively, from a recent nonreversible cell study[29] based on the assumption of null liquid junction potential.[30,31] For *N*-methylacetamide at 0.5 mass fraction in water, we have pK_{AP} = 14.48 at 25 °C

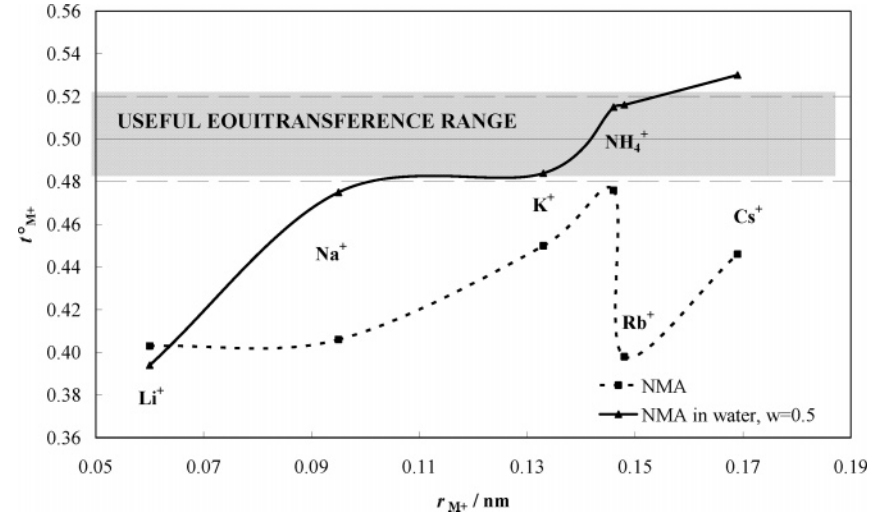

Figure 3. Cationic transference numbers at infinite dilution ($t°_{M+}$) of MCl salts as a function of cationic Pauling's radii (r_{M^+}), in two amidic solvents.

from Asuero et al.[28] and $pK_{AP} = 14.85$ at 20 °C from Halle et al.,[32] but no datum on primary medium effect, and the intersolvental systematization of the relevant pH scale in this solvent is, therefore, impossible.

Singling out Suitable Equitransferent Salt Bridges for the Abatement of Liquid Junction Potentials. Having implemented the acquisition of the pH standards, in order to make pH_X measurements possible in the solvents Z studied here, it is now indispensable to single out and characterize experimentally suitable binary uni-univalent electrolytes MX for insertion as appropriate *equitransferent* salt bridges in the same medium Z of the operational cell {Pt|H_2|unknown pH_X, or standard pH_{PS} [or pH_{SS}] in Z|salt bridge in Z|AgCl|Ag|Pt}, to abate the intervening liquid junction potentials. By analogy with the features of known *aqueous* salt bridges, the MX salts explored here have $M^+ = Li^+$, Na^+, K^+, NH_4^+, Rb^+, and Cs^+ and $X^- = Cl^-$. In the present context, great interest is aroused by *N*-methylacetamide (due to the paucity of data hitherto available for ionic transference numbers t_{M^+}[33]), and particularly by the mixed solvent (*N*-methylacetamide + water) at $w = 0.5$, for which there is a complete lack of data. The method adopted here is based on measuring the emfs of the pair of Helmholtz's cells F and G, and the line of data processing is given in the Introduction.[8,13,14]

Table 8 collects the emf pairs for the cells E_F and E_G as a function of molality pairs m_1 (fixed) and m_2 (varied) of MCl salts, the working temperatures being 303.15 K for *N*-methylacetamide and 298.15 K for (*N*-methylacetamide + water), at molalities $m \leq 0.1$ mol·kg^{-1}. The key feature of the method[13,14] is that only the E_F values are measured, whereas the corresponding E_G values can be calculated according to the equation

$$E_G = 2k \log(m_2\gamma_{\pm,2}/m_1\gamma_{\pm,1})_{MCl} \tag{10}$$

where, for the present purpose, the mean ionic activity coefficients $\gamma_\pm$ of MCl are quantified by the well-known Debye−Hückel equation[20,34−38]

$$\log \gamma_\pm = -A_Z m^{1/2}/(1 + a_0 B_Z m^{1/2}) - \log(1 + 2mM_Z) \tag{11}$$

The ancillary quantities used for eq 11 are also quoted in Table 8. The E_F versus E_G plots are all rectilinear within the MCl molality ranges explored and, as described recently,[13,14] the slopes give directly the limiting cationic transference numbers $t°_{M^+} = dE_F/dE_G$. The $t°_{M^+}$ values found are quoted in Table 8. Assuming the useful range of equitransference for a salt bridge MCl to be expressed as $0.48 < t°_{M^+} < 0.52$, just as is common practice in aqueous electroanalysis, Figure 3 shows beyond doubt that the classical salt bridges KCl, RbCl, and CsCl lose their equitransference levels typical of pure aqueous medium only, and, in conclusion, the present results solidly confirm recent findings,[39] namely, that ammonium chloride is unique in its feature of being applicable as a suitable salt bridge in all amidic and/or (amidic + aqueous) solvent media.

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Received for review December 21, 2006. Accepted June 29, 2007. The financial support of Italy's MIUR (FIRST) is gratefully acknowledged.

JE600581J