REVIEW

Salt bridge in electroanalytical chemistry: past, present, and future

Takashi Kakiuchi

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Abstract A salt bridge is a device indispensable in electroanalytical chemistry and has been used over 100 years. Thanks to a salt bridge, we are able to concentrate our attention to what is happening at the working electrode. However, the magical performance of the traditional salt bridge based on potassium chloride does not always work satisfactorily. The longevity of KCl-type salt bridge is mainly because of the lack of better alternatives. A newly emerged salt bridge based on moderately hydrophobic ionic liquids is promising to solve many of the problems that KCl-type salt bridges are unable to, possibly making the future of electroanalytical chemistry a little easier and brighter.

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Introduction

Any electrochemical cell has at least one liquid junction, that is, the contact of two ionic conductors of different chemical compositions. Even in a cell where the liquid junction appears to be absent, such as a Harned cell,

$$Pt|H_2(g), HCl(aq), AgCl|Ag|Pt' \qquad (1)$$

the composition of the electrolyte solution in the vicinity of the Pt electrode and that in the Ag/AgCl electrode is not strictly the same [1] because the solution on the left-hand side is saturated with H_2, while the solution around the left is not with H_2 but with AgCl. If the latter solution is saturated with H_2, Ag^+ in the solution is thermodynamically reduced to Ag, as exemplified by nanoparticle formation by reduction of Ag^+ with H_2 [2, 3].

To avoid the direct redox reaction of the two redox couples in the solution phase, the separation of two ionic conductors of different compositions is a requirement that should be satisfied in any electrochemical cell. This may be done, to some extent, by inserting a separator between the two solutions. Such a separator cannot, however, remove or minimize the liquid-junction potential at the contact of the two solutions. The magnitude of liquid-junction potential that arises between the two ionic conductors of different compositions is mostly a few tens millivolts at most, but may not be negligible, depending on the purpose of electrochemical measurements. A typical example of

the cases where the liquid-junction potential, or, to be exact, its the change with the solution composition, is not permissible is potentiometry. To overcome the problem of liquid-junction potential, salt bridges made of a concentrated aqueous KCl solution have been used to nullify the liquid-junction potential over 100 years. If it works ideally, the potential of each of the two electrodes in an electrochemical cell is treated independently. It is then justified, without being concerned with the reaction at the other electrode, to use the Nernst equation, the central player in electroanalytical chemistry,

$$E = E^0 + \frac{RT}{nF} \ln \frac{a_{Ox}}{a_{Rd}} \qquad (2)$$

for a half cell reaction at one of the two electrodes,

$$Ox + ne^- \rightleftharpoons Rd \qquad (3)$$

Here, E is the potential of one of the electrodes measured referred to the potential of the other electrode; E^0 is the potential when $a_{Ox} = a_{Rd}$; and R, F, T, and n have the usual meanings.

Unfortunately, however, the function of the traditional salt bridges is not always ideal. The non-ideality of KCl-type salt bridges was known already at the very beginning of the study of liquid-junction potential [4–6] and has plagued electrochemists and others involved with electroanalytical chemistry, in particular potentiometry. In other words, KCl-type salt bridge has survived over 100 years, despite its obvious shortcomings. A new salt bridge made of a moderately hydrophobic ionic liquid, recently proposed as a conceptually new salt bridge [7, 8], is free from the major shortcomings of KCl-type salt bridge and may be able to break up the "vicious circle" [9] of the relationship between the single ion activity and the liquid-junction potential.

The purpose of this article is to provide some basics about salt bridge that is often deemed to be a vexed but essential component in electroanalytical chemistry. This paper is organized as follows: "Historical overview of salt bridge" describes a short history of salt bridge. "Liquid-junction potential and single ion activity" runs through the link between liquid-junction potential and the single ion activity. "Performance of potassium chloride salt bridge" highlights the limitations of KCl-based salt bridge. "Principles of ionic liquid salt bridge" summarizes the basic principle of ionic liquid salt bridge. "Performance of ionic liquid salt bridge" introduces two examples of experimental results, showing the performance of ionic liquid salt bridge. "Future of salt bridges" outlines the issues and prospects of salt bridges. "Conclusions" succinctly describes a view

on the status of salt bridge in the past, present, and future for non-aqueous solvents and mixed solvent are not dealt with in this article. Details on this important subject are described in Izutsu's book [10].

Historical overview of salt bridge

The presence of the liquid-junction potential between two electrolyte solutions was recognized in the end of the nineteenth century [11] and was treated theoretically by Nernst [12, 13] and Planck [14, 15] as well as experimentally by Nernst [13] and Negbauer [16]. In 1895, Tower, then Leipzig, first demonstrated that an aqueous KCl solution nearly cancels out the liquid-junction potential [17, 18]. This idea is based on the knowledge of the mobility of different ionic species, established by Kohlrausch [19] and, later, by Ostwald [20], and the theory of the diffusion potential that develops across a liquid junction [13–15].

Tower's idea was apparently disseminated by *Hand- und Hülfsbuch zur Ausfürung Physiko-chemischer Messungen* published in 1902 [21]. This second edition, mainly revised by Luther, cites Tower's paper published in 1896. As no description about salt bridge is found in the first edition of this book [22], Ostwald and Luther apparently ascribed the originality of the salt bridge to Tower, though they recommended 3.5 normal KCl for a salt bridge, whereas the highest concentration of KCl Tower studied was 1 normal. The idea of salt bridge was further examined by Bjerrum in his papers in 1905 and 1911 [4, 5, 23]. Bjerrum cited the above book for the basic idea of salt bridge, but without mentioning the edition. Henderson's theoretical treatments of diffusion potential assuming the constant concentration gradient model in 1907 [24] and 1908 [25] facilitated the study of the liquid-junction potential. The main driving force of the study of liquid-junction potential at that time was the evaluation of the single electrode potential, which is similar to the present-day standard electrode potential, by eliminating the contribution of the liquid-junction potential to the electromotive force, i.e., the cell voltage [13, 26, 27].

In addition to KCl, other electrolytes were tested for their capability of eliminating the liquid-junction potential. The salts tested include KNO_3, NH_4NO_3, $LiCl$, $NaNO_3$, $Ca(CH_3COO)_2$, KI, and KBr [28–31]. According to Loomis, "potassium chloride is by far the most efficient of the salts used for eliminating contact potential" [30].

After these theoretical and experimental investigations in 30 years spanning over the turn of the century, KCl-based salt bridge was popularized for potentio-

metric determination of pH, potentiometric titration, as well as the study of liquid-junction potentials. Before the salt bridge was known, potentiometric titration was made in the presence of the liquid-junction potential between the sample solution and the reference electrode [32].

Shortly after the publication of the idea of salt bridge and a glass membrane as an ion sensor [33, 34], Haber and Klemensiewitz showed that a glass membrane can be used to measure the change in the acidity of an aqueous solution in potentiometric titration [35]. This paper is known for its demonstration of a glass membrane as a pH-sensitive electrode. It is less conspicuous but their work was also a demonstration of how useful the salt bridge can be in potentiometry, in that they proved, indirectly, the practical usefulness of KCl salt bridge in electroanalytical chemistry. In their cell, the salt bridge was integrated in a reference calomel electrode with a single liquid junction or "half-bridge" [36]; the bridging part was an inverted U-shaped glass tube filled with a 1 normal KCl solution, called "Heber (siphon)".

Their work may be seen as the first attempt of electroanalytical chemistry in the sense that, by using a concentrated (1 normal) KCl, it is shown possible to focus on the indicator electrode, although at that time the main stream of the potentiometric pH measurements was the use of hydrogen electrodes in combination with a KCl bridge [6, 37–40]. After a while, glass electrodes were enthusiastically studied, in combination with a calomel electrode with a liquid junction, for a pH sensor mainly by biochemists and physiologists [41–43].
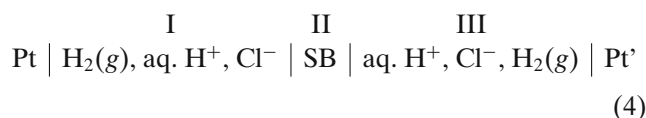
Interestingly, in the early time of the use of a concentrated KCl solution to cancel the liquid-junction potential, the terms "die eingeschalteten Lösung (Inserted solution)" [5], "connecting solution" [29], "connecting vessel" [44], "a Nernst U-tube" [44], "connecting salt solutions" [45], "an interposed saturated solution of potassium chloride" [6], "the connecting siphon" [46], and "connecting liquid" [40] were used depending on the actual method of connecting the two electrolyte solutions. Expressions, "bridge" and "salt bridge", are seen in papers around 1920s by American [37, 47–49] and British [50] researchers.

That the value of the liquid-junction potential depends on the shape and form of the liquid junction and also on time was recognized already at the beginning of the liquid-junction potential studies [5, 23, 44, 47, 51–53]. Bjerrum used a layer of sea sand in the glass tube filled with a KCl solution to stabilize the liquid junction [5]. The flowing junction was proposed as the one to give a stable liquid-junction potential and was employed for the study of the liquid-junction potential [54, 55]. However, this is obviously not a practical so-

lution for the purpose of electroanalytical chemistry. A "conventional" KCl-based salt bridge, a three-weight-percent-agar-gelled saturated KCl solution, used for some time in electroanalytical chemistry, was proposed by Fales and Vosburgh in 1918 [47]. Such an agar-gelled salt bridge ("Agarheber" (agar syphon)) was advocated by Michaelis and his Japanese coworkers [38, 39] to replace the Bjerrum's extrapolation method for canceling the liquid-junction potential in potentiometric pH measurements. For further historical developments of salt bridge and liquid-junction potential up to 1920 and up to 1960, the books by Clark [56] and by Ives and Janz [57], respectively, are useful. Modern aspects on the issues of liquid-junction potential are more recently reviewed by Covington and Rebelo [58].

Liquid-junction potential and single ion activity

It is well-known that both liquid-junction potential and single ion activity are non-thermodynamic quantities. It is also well-known that the difficulty in accurately evaluating the liquid-junction potential is linked to the impossibility of an accurate determination of the single ion activity. But it may be useful to consider the relationship between the two using a simple example. Suppose that we have a following cell,

$$
\overset{\text{I}}{\text{Pt}} \mid \text{H}_2(g), \text{aq. H}^+, \text{Cl}^- \mid \overset{\text{II}}{\text{SB}} \mid \overset{\text{III}}{\text{aq. H}^+, \text{Cl}^-, \text{H}_2(g)} \mid \text{Pt'}
$$

$$(4)$$

where SB stands for a salt bridge. Assuming that the Nernst equation, Eq. 2, holds for two half cell reactions at the electrodes on both sides,

$$
\text{H}^+ + \text{e}^- \rightleftharpoons \frac{1}{2}\text{H}_2 \tag{5}
$$

the cell voltage, E, is given by,

$$
E = \Delta E_{\text{SB}} + \frac{RT}{F} \ln \frac{a_{\text{H}^+}^{\text{III}}}{a_{\text{H}^+}^{\text{I}}} \tag{6}
$$

where ΔE_{SB} is the difference between the two liquid-junction potentials formed on both sides of the salt bridge and $a_{\text{H}^+}^{\alpha}$ is the activity of H$^+$ in phase α (α is either phase I or phase III).

If ΔE_{SB} is negligibly small, it is possible to know the ratio of the activities of H$^+$ from E, but not the absolute value of $a_{\text{H}^+}^{\alpha}$. When the concentration of H$^+$ in one of the phases is lower than 0.1 mmol dm^{-3}, the following

Debye–Hückel limiting law is applicable to calculate the activity coefficient of ions.

$$\log_{10}\gamma_j = -A_c|z_i z_j|\sqrt{I} \tag{7}$$

where $A_c = 0.511$ mol$^{-1/2}$ dm$^{3/2}$ for water at 25 °C and z_i and z_j are the charges on the cation i and anion j, respectively, with the signed unit of electronic charge, and I is the ionic strength. This equation does not contain any adjustable parameters that reflect the nature of a particular ion and is supposed to be applicable to any single ion in low ionic strength solutions. Equation 7 well applies when the ionic strength of an aqueous solution is less than 0.1 mmol dm^{-3}. Once the value of $a_{H^+}^\alpha$ in either phase I or phase III is known, the $a_{H^+}^\alpha$ in the other phase can be calculated from the measured E value.

For this procedure of estimating the single ion activity, the liquid-junction potential between the salt bridge and an aqueous solution, I or III, is not necessarily zero or negligibly small. What is required is a salt bridge that maintains the liquid-junction potential constant, no matter what the composition of the solution in contact is and even when the ionic strength of the solution is low, so that the Debye–Hückel limiting law is applicable. A similar protocol can be applied to estimate the single ion activity of other ions. For example, by inserting an ideal salt bridge in a Harned cell (Eq. 1), it is possible to measure the activity of Cl$^-$.

The single ion activity can thus be estimated resorting to two extra-thermodynamic assumptions, that is, the constant liquid-junction potential and the Debye–Hückel limiting law. The precision of the estimate depends on the precision of the error in eliminating the sum of the liquid-junction potentials at the interfaces I|II and II|III in Eq. 4. For a given value of $a_{H^+}^{I}$, it is seen from Eq. 6 that ΔE_{SB} introduces an error in the estimate of the $a_{H^+}^{III}$ value by a factor, f,

$$f = \exp\left(\frac{F}{RT}\Delta E_{SB}\right), \tag{8}$$

which is 4% at 25 °C when $\Delta E_{SB} = 1$ mV but becomes 21% when $\Delta E_{SB} = 5$ mV. This is the degree of the "viciousness" in the linkage between the single ion activity and the liquid-junction potential [9], that is, the source of "perplexity" Harned encountered [59]. In other words, if we have a salt bridge that suppresses the liquid-junction potential below ±1 mV, we can estimate the single ion activity with the relative error of ±4%. This is not accurate but may be seen as a fairly good measure of the single ion activity.

To date, the best estimates of the single ion activity could be the pH values in aqueous solutions, in particular those of primary pH standards, based on the Harned cell (Eq. 1) [60]. The underlying assumption is the Bates–Guggenheim convention [61], that is, the activity coefficient of Cl$^-$, γ_{Cl^-}, in a solution at an ionic strength I (≤ 0.1) is given by

$$\log_{10}\gamma_{Cl^-} = -\frac{A_c\sqrt{I}}{1 + 1.5\sqrt{I}} \tag{9}$$

no matter the types of coexisting ions in the solution. Despite the absence of a liquid junction in the Harned cell, this is a non-thermodynamic assumption to reach the activity of hydrogen ion.

When the ionic strength is 0.05 mol kg^{-1}, a typical ionic strength of primary pH standards, the values of mean activity coefficient of HCl and KCl at 25 °C are 0.832 and 0.817, respectively, [62]. This difference in the values suggests that the difference in the activity coefficients of hydrogen ion in these two solutions would be greater. It means that the Bates–Guggenheim convention, a non-thermodynamic closure of the vicious circle to create a consistent world of pH measurements, could lead to an error of a few percent in the activity coefficients of hydrogen ion or 0.01 in pH unit in the determination of pH of various buffers. This would exceed the experimental uncertainty for a typical primary pH measurement of a pH buffer chosen as a primary standard of pH, on the order of 0.004 [60], which corresponds to 0.24 mV or 1% error in the activity.

If a concentrated KCl-based salt bridge is sandwiched by a pH buffer and a very dilute hydrochloric acid solution, Eq. 4 would allow the direct determination of the hydrogen ion activity of the pH buffer, as illustrated above, provided that $\Delta E_{SB} \simeq 0$. However, the liquid-junction potential between the KCl-bridge and a dilute aqueous solution is non-negligible (see below). When the ionic strengths of the two solutions adjacent to the salt bridge are high enough, $\Delta E_{SB} \simeq 0$. This type of system has been used for the determination of the operative pH values of buffers [63].

In 1978, Bates wrote, "With some justification, one may take the view that the failure of thermodynamics to offer a guide to the activity has been overemphasized, and that it is not as serious a limitation as it has been considered to be in the past." in his review article entitled "The problems of the single ion activity" [64]. His statement was probably made on the basis of the premises about the above pH conventions he laid out.

Since the Debye–Hückel limiting law is reliable in low ionic strength solutions, what remains for accurately estimating the single ion activity of H$^+$ by use of the above approach is to find a proper salt bridge.

Performance of potassium chloride salt bridge

The liquid-junction potential is not accessible on a thermodynamic basis but can be deduced using the Henderson equation or other theories of diffusion potential. Table 1 summarizes the values of liquid-junction potentials between a saturated KCl solution and a variety of aqueous solutions calculated by Bates [65].

These values are approximate but provide an index of sign and relative magnitude of the liquid-junction potentials [65]. The canceling of the liquid-junction potential with a saturated KCl solution is seen to be only approximate, with an excursion of a few millivolts, depending on the composition of the sample solution. The residual liquid-junction potential becomes greater with decreasing the electrolyte concentration in a sample solution. Note that in a conventional reference electrode, there is only one liquid junction between a saturated or concentrated KCl-salt bridge and a sample solution, and a value in Table 1 is added to the measured cell voltage.

Table 2 Liquid-junction potentials between dilute solutions and a saturated solution of potassium chloride at 25 °C [65, 66]

Concentration mol dm^{-3}	CH$_3$COOH: CH$_3$COONa	KH phthalate	HCl	KOH	KCl
10^{-2}	3.2	3.5	2.9	1.9	2.8
10^{-3}	4.1	4.1	4.0	3.2	3.9
10^{-4}	5.0	4.9	4.8	4.5	5.0
10^{-5}	5.8	5.8	5.7	5.7	6.1
10^{-6}	6.7	6.7	6.7	6.9	7.1

The potential is referred to the inner potential of the dilute aqueous solutions

The performance of the KCl-type salt bridge deteriorates with decreasing the ionic strength of a sample solution. Table 2 shows this tendency, in which the liquid-junction potentials were deduced by Picknett [66] and cited by Bates [65].

It is unfortunate for KCl-type salt bridges that at such low concentrations where the Debye–Hückel limiting law is applicable, the elimination of the liquid-junction potential is far from ideal. For example, an error of 6 mV in a measured cell voltage gives rise to the error in the activity coefficient of about 20%. This is nontrivial. In potentiometric pH measurements, 6 mV translates to 0.1 in pH. This also corresponds to the same magnitude, 20%, of error in the estimate of hydrogen ion activity. The proposition illustrated above using Eq. 4 is thus not workable with a KCl-type salt bridge in a dilute aqueous solution.

There are other problems in using a KCl-type salt bridge in contact with a low ionic strength solution. It takes much longer time before reaching a stable liquid-junction potential. This necessitates long time, for example, in pH measurements. Moreover, during that time, the leakage of KCl into the sample solution can elevate the ionic strength, which may be non-negligible in accurate potentiometry of the pH of low ionic strength samples, such as rain water. Clogging of the junction due to the precipitates of AgCl and possibly Ag at the junction plug is another technical problem when using a KCl-type salt bridge in a low ionic strength solution [67–69].

It has been recognized that the unstable potential and insufficient reduction of the liquid-junction potential with KCl-based salt bridge are particularly problematic in determination of pH of low ionic strength samples [70–74]. After elaborate experiments of measuring pH of low ionic strength solutions, Metcalf concluded in 1987 [75], "Consequently, the assumption of a negligible residual junction potential error in future pH measurements of dilute acid standards is subject to question in accurate work. Further progress in this field

Table 1 Liquid-junction potentials, E_j, at the junction, solution X| saturated KCl calculated from limiting ionic mobility values by the Henderson equation at 25 °C [65]

Solution X, concentration (mol dm^{-3})	E_j (mV)
HCl, 1	14.1
HCl, 0.1	4.6
HCl, 0.01	3.0
KCl, 0.1	1.8
KH$_3$(C$_2$O$_4$)$_2$, 0.l	3.8
KH$_3$(C$_2$O$_4$)$_2$, 0.05	3.3
KH phthalate, 0.05	2.6
KH$_2$ citrate, 0.1	2.7
CH$_3$COOH, 0.05; CH$_3$COONa, 0.05	2.4
CH$_3$COOH, 0.01; CH$_3$COONa, 0.01	3.1
KH$_2$PO$_4$, 0.025; Na$_2$HPO$_4$, 0.025	1.9
NaHCO$_3$, 0.025; Na$_2$CO$_3$, 0.025	1.8
Na$_2$CO$_3$, 0.025	2.0
Na$_2$CO$_3$, 0.01	2.4
Na$_3$PO$_4$, 0.01	1.8
NaOH, 0.1	−0.4
KOH, 0.1	−0.1
KOH, 1	−6.9

Potential is referred to the inner potential in the sample solution

seems limited by the non-availability of technological innovations which provide highly reproducible liquid-junction errors or minimize temperature equilibration errors in pH probes" [75]. No progress has been made, since then, and his statement has remained valid to date. A very recent statistical analysis of the pH values of dilute mineral acid solutions, which had been reported by several groups in the 1980s, confirmed the bias of pH values to the positive side by 0.043 ± 0.007 and ascribed this discrepancy to the residual liquid-junction potential [76].

Principles of ionic liquid salt bridge

A hydrophobic ionic liquid and an aqueous solution form a two-phase system [77, 78]. At the interface between the two phases, a phase-boundary potential develops, as the ions constituting the ionic liquid partition into the aqueous phase [79]. When the ions of the aqueous phase is hydrophilic enough, the dissolution of these ions into the ionic liquid phase is negligible. The phase-boundary potential is then dictated by the distribution potential, regardless of the composition of the aqueous phase and the ionic liquid phase can function as a new type of a salt bridge [7, 79].

The phase-boundary potential between the aqueous phase (W) and the ionic liquid phase (IL) referred to the inner potential of the IL, $\Delta_{IL}^{W}\phi$, is given by

$$\Delta_{IL}^{W}\phi = \frac{1}{2}\left(\Delta_{IL}^{W}\phi_{C^+}^{0} + \Delta_{IL}^{W}\phi_{A^-}^{0}\right) + \frac{RT}{2F}\ln\frac{\gamma_{A^-}^{W}\gamma_{C^+}^{IL}}{\gamma_{C^+}^{W}\gamma_{A^-}^{IL}} \quad (10)$$

where $\Delta_{IL}^{W}\phi_{C^+}^{0}$ and $\Delta_{IL}^{W}\phi_{A^-}^{0}$ are the standard ion transfer potential[1] of the ionic liquid constituent cation, C^+, and anion A^-, and $\gamma_{C^+}^{\alpha}$ and $\gamma_{A^-}^{\alpha}$ are the activity coefficients of i in the phase α ($\alpha = W$ or IL). The nature of $\Delta_{IL}^{W}\phi$ is thermodynamic, unlike the diffusion potential, and $\Delta_{IL}^{W}\phi$ does not depend on the form or the shape of the liquid–liquid contact. For this reason, IL-based salt bridge is conceptually new, distinct from KCl-type salt bridge. The advantages of IL-based salt bridge include the fast response and stability of the liquid-junction potential, in particular even in contact with a low ionic strength solution (see below), the low solubility of the ionic liquid in an aqueous solution, typically less than 1 mmol dm^{-3}, which means less contamination of a sample and longer lifetime of reference electrodes with

much less frequent necessity of refilling the internal solution, and flexibility of designing salt bridges for different purposes thanks to the innumerable variety of ionic liquids.

In actual situations when the salt bridge is working, however, the distribution equilibrium throughout the two phases is rarely established because the diffusion of the C^+ and A^- into the sample solution is slow in comparison with the time scale of measurements. In such a diffusion–migration process, the difference in the mobility of C^+ and A^- in the aqueous phase gives rise to two contributions to the phase-boundary potential; the mixed potential when the electrolyte concentration in the aqueous phase is substantial [80] and the diffusion potential when the concentration of the electrolyte solution is lower than the solubility of the ionic liquid [81]. In the former case, $\Delta_{IL}^{W}\phi$ is given by [80]

$$\Delta_{IL}^{W}\phi = \frac{RT}{2F}\ln\left(\frac{D_{C^+}^{W}}{D_{A^-}^{W}}\right)^{1/2} + \frac{\Delta_{R}^{W}\phi_{C^+}^{0} + \Delta_{R}^{W}\phi_{A^-}^{0}}{2} \quad (11)$$

where $D_{C^+}^{W}$ and $D_{A^-}^{W}$ are the diffusion coefficients of C^+ and A^- in the aqueous phase. In the latter case, the diffusion potential due to the difference in $D_{C^+}^{W}$ and $D_{A^-}^{W}$ is added to the distribution potential [81]. In the absence of the concentration gradient of a 1:1:electrolyte MX in the aqueous phase, the Henderson equation [24] for the diffusion potential takes the form,

$$\Delta\phi_{diff}^{W} = \left(\frac{u_{C^+} - u_{A^-}}{u_{C^+} + u_{A^-}}\right)$$
$$\times \frac{RT}{F}\ln\frac{c_{[C^+][A^-]}^{W}(u_{C^+} + u_{A^-}) + c_{MX}^{W}(u_{M^+} + u_{X^-})}{c_{MX}^{W}(u_{M^+} + u_{X^-})} \quad (12)$$

where $\Delta\phi_{diff}^{W}$ is the diffusion potential in W referred to the electrostatic potential in W at the interface between the IL and W, $c_{[C^+][A^-]}^{W}$ is the solubility of $[C^+][A^-]$, and u_i is the mobility of ion i ($i = M^+$, X^-, C^+ or A^-) in W.

To minimize the contribution of these two potentials, it is desirable to use an ionic liquid that consists of cation and anion having similar mobility values. It is also important to adjust the value of the phase-boundary potential to minimize the interference by other ions in the aqueous phase. The solubility is also an important factor because it determines the electrochemical polarizability of the interface [80]. Practically, the solubility determines the life-time of a ionic liquid salt bridge.

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[1] The standard ion transfer potential of ion j is defined by $\Delta_{IL}^{W}\phi_{z_j}^{0} = -\Delta G_{j}^{IL\rightarrow W,0}/(z_j F)$, where $\Delta G_{j}^{IL\rightarrow W,0}$ is the standard Gibbs energy of the transfer of j from the ionic liquid to water.
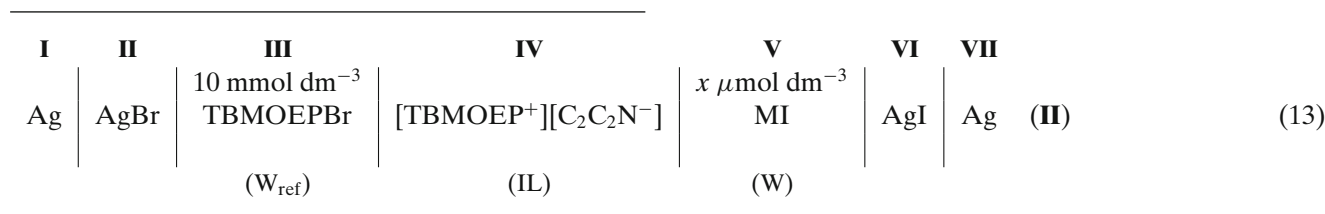
Performance of ionic liquid salt bridge

Constancy of the liquid-junction potential between an ionic liquid and an aqueous solution

To show the feasibility of using an ionic liquid for the salt bridge, a typical moderately hydrophobic ionic liquid, 1-methyl-3-octylimidazolium bis(trifluoromethanesulfonyl)amide ([C8mim$^+$][C$_1$C$_1$N$^-$]) was initially employed [7, 81, 82]. The value of $\Delta_{IL}^{W}\phi$ was demonstrated to remain constant within ± 1 mV over the change in the concentration of HCl, LiCl, NaCl, and KCl between $1.0 \times 10^{-4} \sim 0.2$ mol dm^{-3} [81]. However, at lower ionic strength solutions, $\Delta_{IL}^{W}\phi$ deviated from a constant value at higher concentrations [81]. The main reason for the deviation is the contribution of the diffusion potential because the mobility of C8mim$^+$ is lower than that of C$_1$C$_1$N$^-$. To extend the applicable concentration range to the more diluted solution side so that Eq. 7 is applicable, several ionic liquids were recently synthesized and examined the constancy of the phase-boundary potential [8, 83].

One example of a moderately hydrophobic ionic liquid designed for an IL-based salt bridge is tributyl(2-methoxyethyl)phosphonium bis(pentafluoroethanesulfonyl)amide ([TBMOEP$^+$][C$_2$C$_2$N$^-$]) [8]. The values of limiting molar ion conductivity of the constituent ions, TBMOEP$^+$ and C$_2$C$_2$N$^-$, in water at 25 °C are 25.5 and 26.1 S cm^2 mol^{-1}. Figure 1 shows the cell voltage of the following cell as a function of the mean activity of lithium iodide, sodium iodide, and potassium iodide, at 25.0 °C [8],
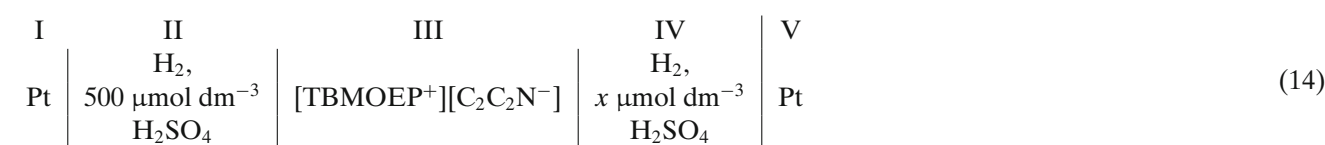
I	II	III	IV	V	VI	VII		
Ag	AgBr	10 mmol dm^{-3} TBMOEPBr (W$_{ref}$)	[TBMOEP$^+$][C$_2$C$_2$N$^-$] (IL)	x μmol dm^{-3} MI (W)	AgI	Ag	(II)	(13)

where TBMOEPBr stands for tributyl(2-methoxyethyl)phosphonium bromide and MI is either LiI, NaI, or KI. The reason for the choice of these electrolytes and Ag|AgI electrode on the right-hand side of the cell is that the solubility of AgCl and AgBr in water complicates the preparation of very dilute solutions on the level of micromoles per cubic decimeter order. The slope of the solid line in Fig. 2 is 59.16 mV. All data points for LiI (circle), NaI (square), and KI (triangle) are on this line, which indicates that the Ag|AgI| aq. I$^-$ electrode Eq. 13 is responsible to the nernstian slope and confirms that the phase-boundary potential between [TBMOEP$^+$][C$_2$C$_2$N$^-$] and the aqueous MI solution remains constant over the change in the concentration of MI from 1,000 down to 1 μmol dm^{-3}.

In comparison with the estimated liquid-junction potential between a saturated KCl salt bridge and a dilute aqueous solution in Table 2, the result in Fig. 1 is very promising for the IL-based salt bridge to maintain the liquid-junction potential constant down to 1 μmol dm^{-3}.

Estimates of pH of dilute sulfuric acid solutions using an ionic liquid salt bridge

To examine the usefulness of IL-based salt bridge for determining the single ion activity, the following cell was constructed (see also Fig. 2) [84]. This is the same as Eq. 4 except H$_2$SO$_4$ instead of HCl.
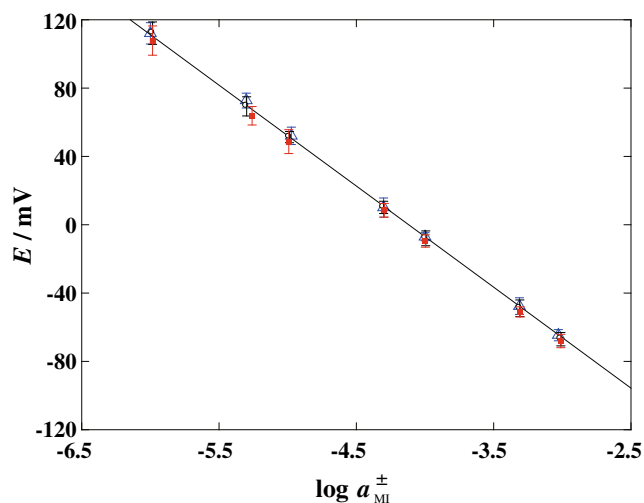
I	II	III	IV	V	
Pt	H$_2$, 500 μmol dm^{-3} H$_2$SO$_4$	[TBMOEP$^+$][C$_2$C$_2$N$^-$]	H$_2$, x μmol dm^{-3} H$_2$SO$_4$	Pt	(14)

Fig. 1 Dependence of E on the common logarithm of the mean activity of LiI (*circle*), NaI (*square*), and KI (*triangle*)) at 25 °C. The *error bars* show 95% confidence intervals calculated from triplicate measurements at each concentration. The *solid line* has the slope of 59.16 mV per decade and is shown as the guide for eyes (after [8]. Copyright: Elsevier; reproduced with permission)

Fig. 2 Illustration of the electrochemical cell with a IL-based salt bridge sandwiched by two hydrogen electrodes. *1* Glass tube for introducing hydrogen gas, *2* hydrogen electrode, *3* glass tube for exhausting hydrogen gas, *4* silicon rubber stopper, *5* U-type glass cell, *6* 500 μmol dm^{-3} H$_2$SO$_4$, *7* x μmol dm^{-3} H$_2$SO$_4$, *8* P$_{444MOE}$C$_2$C$_2$N (after [84]. Copyright: The American Chemical Society; reproduced with permission)

The activity coefficient of H$^+$ in phase II at 500 μmol dm^{-3} was calculated using the Pitzer's model for aqueous sulfuric acid solutions [85]. Experimental pH values, pH$_{exptl}$, at five concentrations of H$_2$SO$_4$ are compared in the sixth column with the calculated pH values, pH$_{calc}$, obtained by the activity coefficients based on Eq. 7. The difference between calculated and experimental values is less than 0.01 at all concentrations. In his meticulous work conducted by Metcalf in 1987 cited above [75], he obtained pH value, 4.06 ± 0.05, from 485 pH measurements of 50 μmol dm^{-3} H$_2$SO$_4$ using a glass electrode in combination with a KCl-based salt bridge. The data in Table 3 are much more accurate with respect not only to the difference between calculated and theoretical values but to the confidence intervals.

There are two more factors to be taken into account in converting a cell voltage to a pH value. First, the solubility of [TBMOEP$^+$][C$_2$C$_2$N$^-$] in water is 0.2 mmol dm^{-3} at 25 °C [8], which can cause the change in the activity of hydrogen ion in phase IV. Second, the slight difference in the mobility values of TBMOEP$^+$ and C$_2$C$_2$N$^-$ gives rise to the diffusion potential in the aqueous phase. The second and third columns in Table 4 list calculated pH values corrected for the first factor and experimental values taking account of the second factor, respectively. The agreement between calculated and theoretical values is significantly better than that in Table 3.
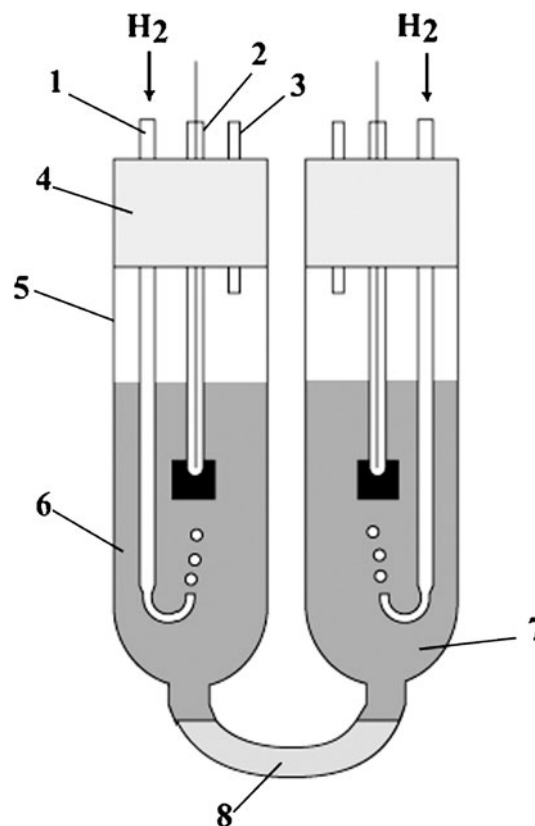
Strictly speaking, there is no way out of the vicious circle in such potentiometry within the framework of thermodynamics. Nevertheless, the results in Tables 3 and 4 are encouraging and strongly suggest that the liquid-junction potential between [TBMOEP$^+$][C$_2$C$_2$N$^-$] and a dilute sulfuric acid solution is constant to the extent of ±0.023 for pH or ±1.3 mV for ΔE_{SB} for 95% confidence interval experimental pH values listed in the sixth column.

In the past, considerable efforts have been made to estimate the single ion activities, assuming the negligible liquid-junction potential or calculating the liquid-junction potential, as introduced above. The IL-based salt bridge offers a simpler, yet more accurate way of estimating single ion activities, among which pH is the most important, and would provide the values to be compared with recently developed theoretical predictions of single ion activities [86–89].

Table 3 Experimental and calculated pH value of 20–200 μmol dm^{-3} H$_2$SO$_4$ [84]

$c_{H_2SO_4}$	$m_{H_2SO_4}$	c_{H^+}	γ_{H^+}	pH$_{cal}$	pH$_{ex}$	pH$_{ex}$−pH$_{cal}$
μmol dm^{-3}	μmol kg^{-1}	μmol kg^{-1}				
20	20.06	40.04	0.9910	4.401	4.410 ± 0.021[a]	0.009
50	50.15	99.85	0.9860	4.007	4.008 ± 0.018[a]	0.001
100	100.30	198.87	0.9804	3.710	3.713 ± 0.026[a]	0.003
150	150.45	297.12	0.9762	3.538	3.543 ± 0.020[a]	0.005
200	200.59	394.67	0.9727	3.416	3.421 ± 0.029[a]	0.005

[a] 95% confidence interval

Future of salt bridges

Ionic liquid-based salt bridges can cover many of the weak points of KCl-type salt bridges, notably the stability in low ionic strength solutions. Accurate determination of pH and other single ion activities can lead to the new dimension in the study of electrolyte solutions. Reevaluation of pH data accumulated in environmental monitoring and other fields will loom into view. Practical advantages of ionic liquid-based salt bridges will make electroanalytical chemistry experiments easier, and cleaner in view of no creeping-up of KCl precipitates during storage. The miniaturization and preparation of solid-state reference electrodes are prospective on the basis of well-designed ionic liquids [82].

Further developments in designing and synthesizing ionic liquids as well as manufacturing them into electrochemical devices are to be made to materialize these expected advantage of ionic liquid salt bridges in a variety of applications. The stability and reproducibility of the liquid-junction potential at the ionic liquid salt bridges are not yet at the level of carefully designed KCl-salt bridges, for example, 0.02 mV for 70 min [63].

Unfortunately, ionic liquid-based salt bridges have one intrinsic weak point. The phase-boundary potential that is created by the dissolution of IL-constituent ions is interfered by hydrophobic ions in a sample solution, as is the case of ion-selective electrodes of liquid-membrane type [90–92]. The presence of ionic

Table 4 Effects of the diffusion potential and change in the ionic strength due to the dissolution of [TBMOEP$^+$][C$_2$C$_2$N$^-$] on experimental pH values [84]

$c_{H_2SO_4}$ H$_2$SO$_4$/μmol dm^{-3}	pH$'_{calc}$	pH$'_{exptl}$	pH$'_{exptl}$−pH$'_{calc}$
20	4.406	4.408	0.002
50	4.010	4.007	−0.003
100	3.712	3.713	0.001
150	3.540	3.544	0.004
200	3.418	3.421	0.003

surfactant at the concentration comparable to or higher than the solubility of the IL-constituent ions can shift the IL-based salt bridge and make it impractical. In pH measurements, a 50-mmol dm^{-3} potassium hydrogen phthalate is one of the most reliable primary standards of pH. Due to the dissolution of moderately hydrophobic biphthalate into the IL-based salt bridge, the phase-boundary potential between C8mimC1C1N and a 50-mmol dm^{-3} phthalate buffer was shifted by ca. 5 mV [93], whereas citrate buffers did not show such interference. Even with the innumerable varieties of ionic liquids, there is little room for designing ionic liquid salt bridges free from the interference by biphthalate dissolution. For the same reason, it would be difficult to find ionic liquid salt bridges that can work satisfactorily in highly concentrated electrolyte solutions.

There are therefore cases where KCl-type salt bridges can work better than ionic liquid salt bridges. A proper choice should be made on the basis, the right salt bridge for the right purpose.

Conclusions

MacInnes noted in 1939, "the use of a salt bridge is a makeshift introducing considerable uncertainty" and "In certain types of measurement, however, they appear, at present at least, to be necessary" [1]. His cogent remarks exactly apply even today. The makeshift has survived this long and a promising substitute has just come in. I do not conceive a day in the near future when a salt bridge becomes unnecessary in electroanalytical chemistry for pH and other measurements. Electroanalytical techniques will continue to be viable methodologies in future in view of simple and well-verified operating principles, cost-effectiveness, low-demanding of natural resources, and handiness. Salt bridge, as an indispensable device in electroanalytical chemistry relying on the Nernst equation, has been used over 100 years and so will it be in a similar time

scale for years to come, by incorporating advances in other fields of science.

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