Characterization of aqueous rubidium chloride as an equitransferent ultraconcentrated salt bridge

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From e.m.f. measurements on the concentration cells $Ag|AgCl|RbCl\ (m)\|RbCl\ (m_f)|AgCl|Ag$ and $Rb{-}amalgam|RbCl\ (m_f)\|RbCl\ (m)Rb{-}amalgam$, the ion and solvent transference numbers have been determined for aqueous RbCl solutions at molalities up to $7\,mol\,kg^{-1}$ over the temperature range from 25 to 55 °C. From the ionic transference numbers found, aqueous RbCl emerges as the most closely equitransferent salt bridge ever characterized. Considering also its high solubility ($7.8\,mol\,kg^{-1}$ at 25 °C), RbCl is recommended as a built-in salt bridge for reference electrodes, in view of replacing the insufficiently equitransferent KCl bridges so far adopted by manufacturers.

1. Introduction

In industrial and laboratory monitoring by direct potentiometry (e.g., pH-metric and pIon-metric controls) it is indispensable practice to insert an equitransferent and concentrated binary salt bridge between the reference electrode solution and the test solution to minimize the intervening liquid junction potential. The justification of this practice was given elsewhere [1–3], and it is well known that the residual liquid junction potentials are the major factor affecting the reliability of pH and pIon measurements [4–6]. This demands the availability and selection of appropriate symmetrical CA salt bridges satisfying the basic requirements of equitransference (i.e., equality of the relevant ionic transference numbers, $\tau_{C+} = \tau_{A-} = 0.5$) and high solubility. (The unlikeliness that unsymmetrical aqueous salts might show appropriate equitransference has already been discussed [7]).

Recently, the inadequacy of the popular aqueous saturated-KCl bridge ($\tau_{K+} = 0.48$, $\tau_{Cl-} = 0.52$; saturation concentration of $4.8\,mol\,kg^{-1}$ at 25 °C) was demonstrated [8], and much more concentrated and more closely equitransferent aqueous salt bridges, such as NH$_4$I, RbBr, RbI, and CsCl were characterized [9, 10], the best of them being CsCl ($\tau_{Cs+} = 0.5025$, $\tau_{Cl-} = 0.4975$; saturation concentration of $11.3\,mol\,kg^{-1}$ at 25 °C). Inspection of available data of infinite-dilution molar conductances of the Rb$^+$ and Cl$^-$ ions [11] suggests that RbCl might also be a promising candidate for the role of salt bridge, and this prompted the present investigation, aimed at ascertaining the equitransference level of aqueous RbCl over the whole range of concentrations and at various temperatures.

The method adopted here combines the electromotive forces (e.m.f.), E_1 and E_2, respectively, of the following concentration cells with transference:

$$Ag|AgCl|RbCl\ (m)\|RbCl\ (m_f)|AgCl|Ag \quad (1)$$

$$Rb_xHg_{1-x}|RbCl\ (m_f)\|RbCl(m)|Rb_xHg_{1-x} \quad (2)$$
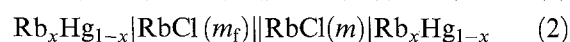
(where Rb_xHg_{1-x} denotes flowing rubidium-amalgam electrodes with rubidium at mole fraction x, and $\|$ the junction between RbCl solutions at molality m_f fixed and m varied), with the e.m.f. E_3 of the corresponding double cell without transference:

$$Rb_xHg_{1-x}|RbCl\ (m_f)|AgCl|Ag{-}$$
$$Ag|AgCl|RbCl\ (m)|Rb_xHg_{1-x} \quad (3)$$
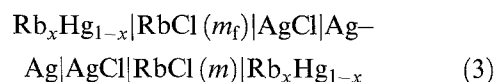
The latter e.m.f., whose expression is

$$E_3 = 2\frac{RT}{F}\ln\left(\frac{m\gamma}{m_f\gamma_f}\right)_{RbCl} \quad (4)$$

(where γ denotes mean molal activity coefficients of RbCl at the relevant molalities) need not be measured because it can be conveniently computed from the available γ data [12, 13].

On thermodynamic grounds, for a given $m - m_f$ gradient, the following relation holds:

$$E_1 + E_2 = E_3 \quad (5)$$

which has, therefore, been used to convert E_2 into E_1 values in order to provide a single data set in terms of E_1 against E_3.

It was shown [14] that

$$dE_1/dE_3 = \tau_{Rb+} - \tau_W M_W m \quad (6)$$

where τ_{Rb+} and τ_W are, respectively, the transference numbers of the Rb$^+$ cation and of the water (moles of water transferred per faraday inside cell from negative pole to positive pole) at the RbCl molality m; $M_W = 0.018\,015\,mol\,kg^{-1}$ is the molar mass of water, and $\tau_W M_W m$ is the solvent-transfer contribution term. τ_{Rb+} in Equation 6 complies with the Stokes–Robinson

[15, 16] equation:

$$\tau_{Rb^+} = [\lambda^o_{Rb^+} - \tfrac{1}{2}B_2\sqrt{m}/(1 + a_0B\sqrt{m})/$$

$$[\Lambda^o_{RbCl} - B_2\sqrt{m}/(1 + a_0B\sqrt{m})]$$

$$= [\tau^o_{Rb^+} - 0.5]/\{1 - B_2\sqrt{m}/$$

$$[(1 + a_0B\sqrt{m})\Lambda^o_{RbCl}]\} + 0.5 \qquad (7)$$

where $\tau^o_{Rb^+} = \lambda^o_{Rb^+}/\Lambda^o_{RbCl}$ is the limiting (infinite dilution) transference number of cation Rb^+, B_2 and B are classical constants of the Debye–Hückel–Onsager theory, a_0 is the ion–size parameter of RbCl, and $\lambda^o_{Rb^+}$ and Λ^o_{RbCl} are the limiting molar conductances of Rb^+ and RbCl, respectively. The water transference number τ_W can be expressed [9, 14] as

$$\tau_W = \tau^o_W(1 - hM_Wm) \qquad (8)$$

where τ^o_W is the limiting (infinite dilution) transference number of water, and $h = h_{Rb^+} + h_{Cl^-}$ is the primary hydration number of RbCl.

Elaborating upon Equations 6 to 8, τ_{Rb^+} and τ_W values as a function of RbCl concentration are obtained at each temperature of experiment (see Tables 2 and 3) and the result is the characterization of RbCl as a quasi-ideal salt bridge.

2. Experimental details

The rubidium amalgams, to be operated as flowing rubidium amalgam electrodes in cell 2 (Equation 2), were prepared by the same electrolytic method and the same all-glass apparatus already described by Mussini *et al.* [13, 17]. The same mole fraction x of rubidium was fed to the pair of amalgam electrodes,

so that the e.m.f. cell 2 was independent of x. The AgCl electrodes in cell 1 (Equation 1) were prepared by the bielectrolytic method [18]. To deal with the known effect of increasing solubilization of AgCl with increasing molality of alkali chlorides [19], the e.m.f. of cell 1 was measured only at m not exceeding $1\,mol\,kg^{-1}$. The potentiometric, as well as the thermostatic, apparatus was described earlier [17]. All solutions were prepared by weight from redistilled deionized water and Aldrich 99.99%-pure RbCl. The junction between the two RbCl solutions in cells 1 and 2 was made through a three-way tap arrangement ensuring optimum conditions of stability and reproducibility, as done in recent work on the CsCl, KCl, RbBr, RbI and NH_4I bridges [8–10].

3. Results and discussion

Table 1 collects the results of E_1 and E_2 measurements as a function of RbCl molality up to $m = 7\,mol\,kg^{-1}$ over the temperature range from 25 to 55 °C, together with the relevant E_3 values calculated from Equation 4 and the available γ values [12, 13]. For $m > 1\,mol\,kg^{-1}$ at 40 and 55 °C, γ values for RbCl are not directly available, but the corresponding curves of the available molal osmotic coefficients ϕ against m [20] at $m \leq 5\,mol\,kg^{-1}$ are substantially coincident with that at 25 °C. In other words, considering the functional relation between γ and ϕ [21], one can safely assume:

$$(\gamma/\gamma_f)_{25\,°C} = (\gamma/\gamma_f)_{40\,°C} = (\gamma/\gamma_f)_{55\,°C} \qquad (9)$$

which allows computation of γ at 40 and 55 °C at $m > 1\,mol\,kg^{-1}$ since the corresponding γ_f values at

Table 1. E.m.f.s E_3 and E_1 of cells 3 and 1, respectively, at various temperatures θ and molalities m of aqueous RbCl, with corresponding mean-molal activity coefficients γ: m_f and γ_f denote the fixed molality and the corresponding activity coefficient in the above cells

$\theta/°C$	25			40			55		
$m_f/mol\,kg^{-1}$	0.1			0.1			0.1		
γ_f	0.764			0.758			0.751		
$m/mol\,kg^{-1}$	γ	E_3/V	$E_1\backslash V$	γ	E_3/V	E_1/V	γ	E_3/V	E_1/V
0.01	0.900*	−0.10990	−0.05496	0.898*	−0.11512	−0.05713	0.895*	−0.12030	−0.06073
0.02	0.868*	−0.07614	−0.03802	0.864*	−0.07980	−0.03992	0.860*	−0.08336	−0.04126
0.03	0.845*	−0.05669	−0.02822	0.841*	−0.05937	−0.02967	0.836*	−0.06203	−0.03158
0.05	0.813*	−0.03242	−0.01654	0.808*	−0.03396	−0.01685	0.803*	−0.03542	−0.01766
0.2	0.711*	-0.03192	0.01615	0.703*	0.03334	0.01669	0.695*	0.03482	0.01750
0.5	0.639*	0.07352	0.03672	0.630*	0.07688	0.03863	0.619*	0.08009	0.04035
0.5	0.639*	0.07352	0.03708‡	0.630*	0.07688	0.03922‡	0.619*	0.08009	0.04082‡
0.5				0.630*	0.07688	0.03918‡	0.619*	0.08009	0.03969‡
1.0	0.589*	0.10495	0.05307	0.579*	0.10973	0.05530	0.566*	0.11423	0.05748
1.0	0.589*	0.10495	0.05234‡	0.579*	0.10973	0.05599‡	0.566*	0.11423	0.05770‡
1.0				0.579*	0.10973	0.05424‡			
2.0	0.546†	0.13667	0.06779‡	0.538§	0.14318	0.07277‡	0.529§	0.14961	0.07526‡
2.0				0.538§	0.14318	0.07180‡			
3.0	0.536†	0.15656	0.07862‡	0.528§	0.16405	0.08341‡	0.519§	0.17146	0.08683‡
4.0	0.537†	0.17144	0.08564‡	0.529§	0.17968	0.09053‡	0.520§	0.18784	0.09440‡
5.0	0.544†	0.18357	0.09207‡						
7.0	0.564†	0.20271	0.10162‡						

* from ref [13]
† from [12]
§ from [13] and Equation 9
‡ E_1 values obtained from corresponding E_2 values through Equation 5.
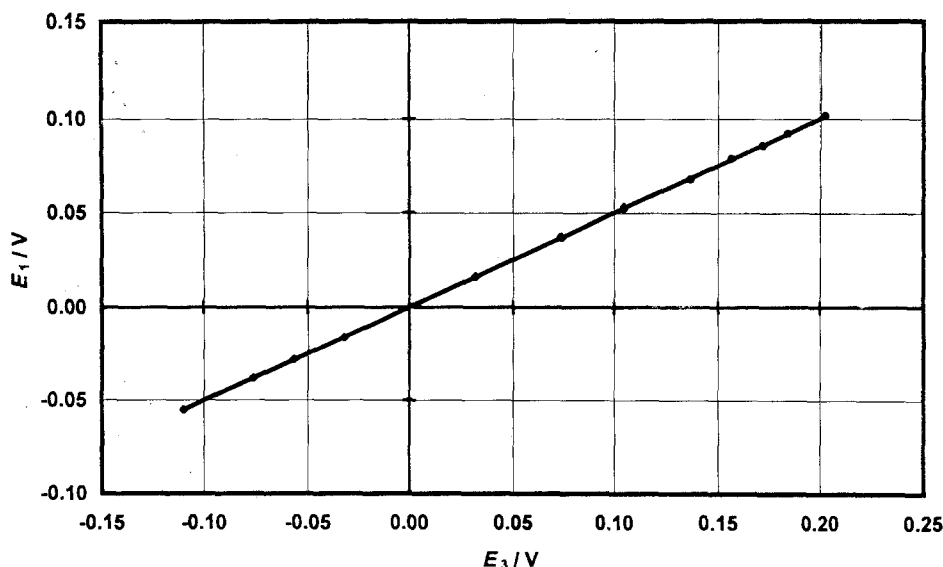
Fig. 1. Linear dependence of the e.m.f. E_1 of the transference cell (1) on E_3 of the cell (3) for aqueous RbCl at 25 °C: $E_1 = 0.50071\ E_3$. (◆) From cell (1) with AgCl electrodes; (●) From cell (2) with rubidium amalgam electrodes (cf. Equation 5).

$m_f = 0.1\ \mathrm{mol\,kg^{-1}}$ are known from the work by Longhi et al. [13].

As shown by the example in Fig. 1, the E_1 against E_3 relation is rigorously linear over the whole range of RbCl molalities, that is, remembering that $E_1 = 0 = E_3$ when $m = m_f$, one can write

$$E_1 = aE_3 \qquad (10)$$

where the slope a turns out to be very close to 0.5. Now, considering Equations 6, 9 and 10, it is clear that

$$dE_1/dE_3 = \tau_{Rb^+} - \tau_W M_W m = \tau^o_{Rb^+} = a \qquad (11)$$

and the deviations of τ_{Rb^+} from the limiting value $\tau^o_{Rb^+}$ depend only on the τ_W values which, in turn, are a function of the molality m and of the primary hydration number h of RbCl through Equation 8. Combining Equations 6–8 and 10, by a procedure of multiple linear regression described in a recent paper [9] and taking $h = h_{Rb^+} + h_{Cl^-} = 5$ [22], τ_{Rb^+}, τ_W, and τ^o_W have been optimized using an appropriate statistical package [23] which also gives the relevant regressional standard errors δ quoted in Tables 2 and 3. The other ancillary quantities required by the above equations are available from the literature: a_o [13], and B, B_2 and Λ^o [11, 24].

The results for τ_{Rb^+} and τ_W are collected in Tables 2 and 3. As implied by the form of the Stokes–Robinson equation (Equation 7) since $\tau^o_{Rb^+}$ is imperceptibly greater than 0.5 (in detail: $\tau^o_{Rb^+} = 0.5007$, 0.5014 and 0.5037 at 25, 40 and 55 °C, respectively), τ_{Rb^+} increases (with respect to $\tau^o_{Rb^+}$) almost imperceptibly with increasing m_{RbCl}; furthermore, the zero-close values of τ_W (cf. Table 3) have negligible effect in Equation 6. τ_W, however small, decreases with increasing m_{RbCl} as expected. The accurate value for the infinite-dilution molar conductivity of the Cl⁻ ion being $76.35\ \mathrm{S\,cm^2\,mol^{-1}}$ at 25 °C [25–27], that of the Rb⁺ ion is $76.56\ \mathrm{S\,cm^2\,mol^{-1}}$ since $\tau^o_{Rb^+} = 0.5007$.

Some applied features of the RbCl bridge are worth consideration:

(i) RbCl has physico-chemical characteristics similar to those of KCl and can be handled in exactly the same manner. Consequently no difficulties will arise to the manufacturer and to the user, apart from the cost of RbCl, which is about eight times more expensive than KCl, at 99.9% purity

Table 2. Transference numbers τ_{Rb^+} of aqueous Rb^+ ion as a function of RbCl molality m_{RbCl} at various temperatures Θ, with respective standard errors δ

$m_{RbCl}/\mathrm{mol\,kg^{-1}}$	$\Theta/°C$		
	25 τ_{Rb^+}	40 τ_{Rb^+}	55 τ_{Rb^+}
0*	0.5007	0.5014	0.5037
0.001	0.5007	0.5014	0.5037
0.002	0.5007	0.5014	0.5037
0.003	0.5007	0.5015	0.5037
0.005	0.5007	0.5015	0.5038
0.007	0.5007	0.5015	0.5038
0.01	0.5007	0.5015	0.5038
0.02	0.5007	0.5015	0.5039
0.03	0.5008	0.5015	0.5039
0.05	0.5008	0.5015	0.5040
0.07	0.5008	0.5015	0.5040
0.1	0.5008	0.5016	0.5041
0.2	0.5008	0.5016	0.5042
0.3	0.5008	0.5016	0.5043
0.5	0.5008	0.5017	0.5044
0.7	0.5008	0.5017	0.5045
1	0.5009	0.5018	0.5046
2	0.5009	0.5018	0.5047
3	0.5009	0.5019	0.5049
4	0.5009	0.5019	0.5049
5	0.5009		
6	0.5009		
7	0.5009		
δ	±0.0006	±0.0012	±0.0009

* Infinite dilution.

Table 3. Water transference numbers τ_W as a function of RbCl molality m_{RbCl} at various temperatures Θ, with respective standard errors δ

m_{RbCl}/mol kg^{-1}	Θ/°C		
	25 τ_W	40 τ_W	55 τ_W
0*	0.0041	0.0121	0.0321
0.001	0.0041	0.0121	0.0321
0.002	0.0041	0.0121	0.0321
0.003	0.0041	0.0121	0.0321
0.005	0.0041	0.0121	0.0321
0.007	0.0041	0.0121	0.0321
0.01	0.0041	0.0121	0.0321
0.02	0.0041	0.0121	0.0321
0.03	0.0040	0.0121	0.0320
0.05	0.0040	0.0121	0.0320
0.07	0.0040	0.0121	0.0319
0.1	0.0040	0.0120	0.0318
0.2	0.0040	0.0119	0.0316
0.3	0.0040	0.0118	0.0313
0.5	0.0039	0.0116	0.0307
0.7	0.0038	0.0114	0.0302
1.0	0.0037	0.0111	0.0295
2.0	0.0034	0.0103	0.0272
3.0	0.0032	0.0096	0.0253
4.0	0.0030	0.0089	0.0236
5.0	0.0028		
6.0	0.0026		
7.0	0.0025		
δ	±0.0005	±0.0014	±0.0044

* Infinite dilution.

level. This greater cost is, however, not prohibitively high and, moreover, it would not be the main component of cost in the production of calomel, silver chloride, or thallium(I) chloride reference electrodes with built-in RbCl bridges. Further, the attainment of substantially greater precision in pH and pIon measurements is too important to be rejected in view of greater production costs. In this context, it is worthwhile to underline that 99.99% pure RbCl is not strictly necessary. In fact, for the present context, the significant impurities in high quality RbCl are K$^+$ and Na$^+$. Analysis of data through the popular Henderson equation [6, 28] shows that a presence of KCl at <0.5% level in RbCl would cause no significant variation in the efficacy of the latter salt bridge in reducing liquid junction potentials E_J. The same is true for a presence of NaCl at < 0.05% level. This means that 99.5% pure RbCl could be used with no drawback, and, more importantly, passing from 99.99 to 99.5% purity would reduce the RbCl cost to about one quarter.

(ii) Aqueous RbCl bridges can be operated at the same concentrations as the popular KCl bridges, for example, 0.1, 1, 3, 3.5, 4 and 4.8 mol kg^{-1} (saturated KCl at 25 °C), but for RbCl there is available another 3 mol kg^{-1} 'reserve' to reach its saturation at 25 °C (~7.8 mol kg^{-1}) which can 'upgrade' the RbCl bridge with respect to

KCl. At any of the above concentrations, RbCl is superior to KCl in reducing liquid junction potentials. It is well known that the worst situation for a salt bridge is that of working at a junction with a strong acid or a strong base. For pH measurements, the IUPAC-endorsed operational equation [29] assumes perfect zeroing of the intervening liquid junction potential E_J by the salt bridge. In other words, E_J is officially ignored but E_J is never exactly zeroed, so that it becomes an important, albeit hardly assessable, component of the pH-metric uncertainty. Let us then consider the junction HCl $(c_A \| KCl (c_s)$, where $c_s = 4.2$ mol dm^{-3} $(= 4.8$ mol kg^{-1} at 25 °C). A first approximation evaluation of E_J can be performed through the Henderson equation [6, 28] which is, however, generally relied upon only at concentrations < 0.1 mol dm^{-3} because it assumes ideality of the electrolyte solutions involved (in fact it would give only the 'ideal part' of E_J) and invariancy of ionic mobilities (ionic conductivities) with varying concentration. With $c_A = 0.001, 0.01$ and 0.1 mol dm^{-3} (molarities instead of molalities are actually required by the Henderson equation) it would turn out that $E_J = 3.7$, 3.0 and 4.7 mV, respectively, corresponding to errors of 0.06, 0.05 and 0.08 in pH (or about -14.1, -11.7, and -17.9% in the H$^+$ concentration c_A), respectively. It should be noted that at the upper c_A here considered for HCl, the salt bridge concentration c_s is forty-two times as great. Now, replacing KCl by RbCl, again at $c_s = 4.2$ mol dm^{-3}, reduces E_J to -0.2, 0.4 and 3.1 mV $(= -0.003, 0.007$ and 0.05 in pH; or 0.8, -1.6 and -12.1% in c_A), respectively. And using saturated RbCl $(c_s = 6$ mol dm^{-3}) the E_J reduction is even more radical. Similar conclusions are arrived at passing from pH to pIon measurements, considering, for example, the parallel junction NaCl $(c_A) \| KCl$ $(c_S = 4.2$ mol dm$^{-3})$. With again $c_A = 0.001$, 0.01 and 0.1 mol dm^{-3} the results are $E_J = 4.2, 3.0$, and 1.5 mV, respectively, corresponding to 0.07, 0.05 and 0.03 in pNa (or -16.4, -11.7 and -5.9% in Na$^+$ concentration). Replacing 4.2 M KCl by 4.2 M RbCl would reduce E_J to -0.3, -0.3, and -0.6 mV, corresponding to errors of only -0.005, -0.005, and -0.01 in pNa $(= 1.2, 1.2,$ and 2.3% in Na$^+$ concentration). These calculations are based on the following values of infinite-dilution ionic conductivities: 350.15, 50.10 and 73.50 S cm^2 mol^{-1} for H$^+$, Na$^+$ and K$^+$, respectively [11]. The reliability of the above E_J values is admittedly incomplete, and no improvement can be expected due to lack of an appropriate and recognized scheme of evaluation of the complementary 'nonideal part' of E_J.

(iii) The typology of salt bridge $\|$ sample junctions was appropriately focused by Guggenheim [30], Covington [31] and Bates [3]. All possible

pH-metric or pIon-metric requirements cannot be satisfied by one type of junction involving one concentration of the salt bridge. Radically different types of junctions (and different designs of cells and reference electrodes) may be required. The finite small leak rate produced by a head of salt bridge solution is essential (e.g., to obtain stable pH readings in dilute, poorly buffered aqueous samples). But this would be inacceptable when no contamination by Cl^- ions is a strict condition, and interposition of a compatible, second salt bridge might become essential. The selection criteria both for the type of RbCl‖sample junction and the cell design are exactly the same as for the KCl‖sample junction.

4. Conclusions

The results for τ_{Rb^+} (cf. Table 2) characterize aqueous RbCl as a quasi-ideally equitransferent salt, indeed the most closely equitransferent one hitherto found. Since the solubility of aqueous RbCl is $7.8\,mol\,kg^{-1}$ at 25 °C, that is, much higher than that of KCl, RbCl must be recommended as an optimal ultraconcentrated equitransferent salt bridge for replacement of the inadequately equitransferent KCl hitherto generally incorporated into the reference electrode design by the manufacturers. On account of the above characteristics, RbCl would be comparatively much more effective in reducing residual liquid junction potentials in, for example, pH measurements on strongly acidic, strongly alkaline, or high-salinity samples.

Acknowledgement

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