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Characterization and use of aqueous caesium chloride as an ultra-concentrated salt bridge

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Five strong aqueous binary electrolytes – one symmetrical (CsCl) and four unsymmetrical (Li_2SO_4, K_2SO_4, Rb_2SO_4, Cs_2SO_4) – have been examined, for possible use as salt bridges for the minimization of liquid junction potentials (E_L), up to the highest concentrations practicable, by the method of homoionic transference cells: $\text{Pt-Ir}|Cl_2|CsCl\ (m_2)\,\|\,CsCl\ (m_1)|Cl_2|\text{Pt-Ir}$ and $Hg|Hg_2Cl_2|CsCl\ (m_2)\,\|\,CsCl\ (m_1)|Hg_2Cl_2|Hg$ for CsCl, and $Hg|Hg_2SO_4|Me_2SO_4\ (m_2)\,\|\,Me_2SO_4\ (m_1)|Hg_2SO_4|Hg$ for the Me_2SO_4 sulphates where Me = Li, K, Rb and Cs. CsCl, K_2SO_4, Rb_2SO_4, and Cs_2SO_4, prove to belong to the class obeying close equality of transference numbers for their ions, that is, $t_+ = |t_-| = 0.5$, over the whole concentration range (namely, from infinite dilution up to saturation). This result qualifies aqueous CsCl as an unrivalled salt bridge, whose equitransference is obeyed more stringently than any other salt. This is now demonstrated experimentally over the whole molality range, the saturation molality being as high as 11.30 mol kg^{-1} at 25° C. The observed property $t_+ = |t_-| = 0.5$ excludes K_2SO_4, Rb_2SO_4, and Cs_2SO_4, as possible salt bridges because the equitransference conditions for minimization of E_L's are $\tau_+ = |\tau_-| = 1/(z_+ + |z_-|) = 0.333$, i.e., $t_+ = 0.333$ and $t_- = 2t_+ = 0.667$. Finally, Li_2SO_4, though behaving quite differently from the other three sulphates studied, does not sufficiently approach the required conditions, contrary to what one might have hoped from its known infinite-dilution transference numbers.

1. Introduction

Very frequently the electrochemist and the electroanalyst have to resort to the well-known practice of inserting a 'concentrated equitransferent' binary electrolyte as a salt bridge at the junction between two electrolyte solutions in order to minimize (if not entirely eliminate) the inevitable liquid junction potential arising therein. However, in doing so, several difficulties and limitations may be encountered; for instance:

(a) regrettably few such electrolytes have hitherto been characterized for use as salt bridges and, practically, these exist only for aqueous solutions;

(b) such electrolytes (for example, the popular KCl, KNO_3, NH_4NO_3, NH_4Cl) do not exactly satisfy the equitransference (that is, equality of transference number for cation and anion: $\tau_+ = |\tau_-| = 1/(z_+ + |z_-|)$ [1–3]) required for a salt bridge. Certain mixtures, such as KCl + KNO_3, have even been proposed [4] as more properly equitransferent salt bridges than KCl or KNO_3 alone;

(c) the highest concentration attainable by each of these, that is, the saturation concentration, which for aqueous KCl at 25° C amounts to 4.804 mol kg^{-1}, may be insufficient to minimize the liquid junction potential if the ionic strength of the solution encountered at the junction (especially if strongly acidic or alkaline) is of the order of 1 mol kg^{-1} or more;

(d) there may be chemical incompatibility between the ions of the salt bridge and those of the two solutions at the junction, for example, with formation of an insoluble salt. This may require insertion of a second compatible salt bridge in contact with the first, usually built-in with the reference electrode (the 'double junction' technique often used with certain ion-selective electrode cells). This makes it necessary to characterize new alternative salt bridges;

(e) an even more urgent need exists of characterizing new salt bridges in non-aqueous or mixed solvents, where the knowledge of equitransferent binary electrolytes is virtually nil.

The present work was prompted by points (a) to (d) above and, upon studying both symmetrical (CsCl) and unsymmetrical electrolytes (Li_2SO_4, K_2SO_4, Rb_2SO_4, Cs_2SO_4), it concludes with the recognition of CsCl as an outstanding, but hitherto ignored, salt bridge having better equitransference, and capable of reaching far higher saturation concentrations (for example, 11.30 mol kg^{-1} at 25° C, 13.31 at 55° C, and 15.45 at 90° C) than most of the salt bridges hitherto used [5]. Thus, CsCl has definite operational advantages over the popular KCl salt bridge in that it is suitable to electrochemical or electroanalytical

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Table 1. Values of E and E_{max} of the cell $Hg|Hg_2SO_4|Me_2SO_4\ (m_2)\ \|\ Me_2SO_4(m_1)|Hg_2SO_4|Hg$ at various m_2 molalities of aqueous Me_2SO_4 but fixed $m_1 = 0.1\ mol\,kg^{-1}$ at 25° C, for Me = K, Rb, Cs. Literature values [15] of the infinite-dilution transference number ($\tau^0_{Me+} \equiv t^0_{Me+}$) of the Me^+ ion are also compared with the slope b of the $E = bE_{max}$ straight line

K_2SO_4			Rb_2SO_4			Cs_2SO_4		
$m_2\ (mol\,kg^{-1})$	$E\ (V)$	$E_{max}\ (V)$	$m_2\ (mol\,kg^{-1})$	$E\ (V)$	$E_{max}\ (V)$	$m_2\ (mol\,kg^{-1})$	$E\ (V)$	$E_{max}\ (V)$
0.1	0.00000	0.00000	0.1	0.00000	0.00000	0.1	0.00000	0.00000
0.3	0.01437	0.02956	0.2	0.00964	0.01955	0.2	0.00983	0.02002
0.5	0.02056	0.04225	0.6	0.02385	0.04838	0.4	0.01898	0.03874
0.7	0.02439	0.05018	1.2	0.03239	0.06573	0.6	0.02423	0.04945
–	–	–	–	–	–	1.4	0.03552	0.07259
–	–	–	–	–	–	1.8	0.03924	0.07991
b	0.4863 ± 0.0002			0.4929 ± 0.0001			0.4902 ± 0.0003	
τ^0_{Me+}	0.4851			0.4930			0.4912	

Table 2. Values of E and E_{max} at 25° C of the cell $Pt\text{-}Ir|Cl_2|CsCl\ (m_2)\ \|\ CsCl\ (m_1)|Cl_2|Pt\text{-}Ir$, and of the equivalent cell $Hg|Hg_2Cl_2|CsCl\ (m_2)\ \|\ CsCl\ (m_1)|Hg_2Cl_2|Hg$ (designated by (a)), at various molalities m_2 of aqueous CsCl with fixed $m_1 = 0.009999\ mol\,kg^{-1}$, with the corresponding transference numbers τ_{Cs+} of the Cs^+ ion and τ_w of the water. Values at infinite dilution ($\tau^0_{Cs+} \equiv t^0_{Cs+}$) are compared with the slope b of the $E = bE_{max}$ straight line

$m_2\ (mol\,kg^{-1})$	$E\ (V)$	$E_{max}\ (V)$	τ_{Cs+}	τ_w
0.000998	−0.05750a	−0.11513	0.5018	0.0080
0.002000	−0.04020a	−0.07975	0.5018	0.0080
0.005000	−0.01720a	−0.03409	0.5018	0.0080
0.009999	0.00000	0.00000	0.5018	0.0080
0.04977	+0.03839a	0.07685	0.5018	0.0079
0.05000	0.03790a	0.07709	0.5019	0.0079
0.09457	0.05395a	0.10661	0.5019	0.0079
0.09600	0.05375a	0.10725	0.5119	0.0079
0.10075	0.05448a	0.10952	0.5119	0.0079
0.49955	0.09110a	0.18086	0.5021	0.0077
0.50240	0.09110a	0.18115	0.5021	0.0077
0.9628	0.10682a	0.20941	0.5022	0.0075
0.9995	0.10676*	0.21105	0.5022	0.0075
1.0002	0.10602a	0.21109	0.5022	0.0075
1.9998	0.12257a	0.24175	0.5023	0.0070
2.0001	0.12205a	0.24176	0.5023	0.0070
2.0004	0.12282	0.24177	0.5023	0.0070
2.9818	0.13080a	0.26038	0.5023	0.0065
2.9984	0.13170a	0.26067	0.5023	0.0065
2.9998	0.13205	0.26069	0.5023	0.0065
3.9996	0.13886	0.27493	0.5024	0.0061
4.0004	0.13884	0.27494	0.5024	0.0061
4.0038	0.13688a	0.27499	0.5024	0.0061
4.9575	0.14362a	0.28607	0.5024	0.0056
4.9972	0.14454	0.28648	0.5024	0.0056
4.9996	0.14417a	0.28651	0.5024	0.0056
5.9984	0.14934	0.29651	0.5024	0.0051
6.9983	0.15355	0.30529	0.5025	0.0046
8.0023	0.15735	0.31291	0.5025	0.0042
9.0009	0.16058	0.31977	0.5025	0.0037
9.9945	0.16311	0.32566	0.5025	0.0032
10.9992	0.16534	0.33099	0.5025	0.0027
10.9995	0.16442**	0.33099	0.5025	0.0027
b			0.5020 ± 0.0006	
τ^0_{Cs+} (this work)			0.5018 ± 0.0006	
τ^0_{Cs+} (from [16])			0.5030	

* Mean of 4 cells. ** Mean of 5 cells.

applications over a much larger range of ionic strengths of sample solutions, including such special cases as physiological solutions, sea waters, industrial brines, etc. The experimental basis for the present research was the e.m.f. measurement at 25° C of the following homoionic transference cells (all with constant molality m_1 while varying m_2):

$$\mathrm{Hg}|\mathrm{Hg_2SO_4}|\mathrm{Me_2SO_4}\ (m_2)\ \|\ \mathrm{Me_2SO_4}\ (m_1)|\mathrm{Hg_2SO_4}|\mathrm{Hg} \qquad (1)$$

for aqueous Me_2SO_4 where Me = Li, K, Rb, and Cs; and

$$\mathrm{Pt\text{-}It}|\mathrm{Cl_2}|\mathrm{CsCl}\ (m_2)\ \|\ \mathrm{CsCl}\ (m_1)|\mathrm{Pt\text{-}Ir} \qquad (2)$$

combined with

$$\mathrm{Hg}|\mathrm{Hg_2Cl_2}|\mathrm{CsCl}\ (m_2)\ \|\ \mathrm{CsCl}\ (m_1)|\mathrm{Hg_2Cl_2}|\mathrm{Hg} \qquad (3)$$

for aqueous CsCl. The relevant results are summarized in Tables 1 and 2. Those concerning Li_2SO_4 are the same reported in the preceding paper [1], where they were analyzed together with those for HCl to verify the validity of a scheme of basic correlations between ion transport, solvent transport, and ion solvation parameters.

2. Experimental details

The conventional Stokes and Levien's design [6–8] was used for the three cells above, with appropriate modifications to permit the entry and exit of chlorine gas in the case of Cell (2). The structure of the chlorine electrodes was as designed and developed earlier in these laboratories by Faita, Longhi and Mussini [9], the metal support for the Cl_2/Cl^- redox couple being a Pt-Ir 45% alloy on tantalum base, which was not corroded by this aggressive redox couple [9]. Chlorine was diluted with nitrogen at 1 : 99 pressure ratio, in order to make the association of Cl_2 with Cl^- to form Cl_3^- negligible. The Hg_2SO_4 electrodes for Cell (1) were prepared in the same manner as in recent work [10].

The calomel (Hg_2Cl_2) electrodes for Cell (3) were of conventional design [11]. All the Me_2SO_4 and CsCl solutions were prepared by weight from reagent grade chemicals and redistilled deionized water. Temperature control and the potentiometric measuring apparatus were exactly as described earlier [12].

3. Results and discussion

The two e.m.f. sets resulting from measurements on the equivalent Cells (2) and (3) were consistent with each other and were amalgamated into one set for the subsequent data processing.

A feature common to CsCl, K_2SO_4, Rb_2SO_4, and Cs_2SO_4, is that the correlation between the e.m.f., E, of the pertinent transference cell and the corresponding e.m.f., $E_{\max}$, (which implies the limiting conditions $\tau_+ = 1$ for the cation and $\tau_w = 0$ for water, and requires knowledge of the mean molal activity coefficients of the electrolyte concerned with to calculate $E_{\max}$ (see preceding paper [1], Equation 10) is represented by the straight line:

$$E = bE_{\max} \tag{4}$$

As shown by Tables 1 and 2, the values of the slope of such straight lines (see preceding paper [1], Equation (11)):

$$b = \mathrm{d}E/\mathrm{d}E_{\max} = \tau_+ + n_- z_- \tau_w M_w m_2 \tag{5}$$

are all close to 0.5 and coincident, within experimental error, with the infinite-dilution value, τ_+^0, of the pertinent cation transference number. This striking constancy of $\tau_+ \simeq 0.5$ over the whole concentration range (from infinite dilution to saturation) is, however, of paramount importance only for CsCl, which is thereby qualified as an appropriate salt bridge, in contrast with K_2SO_4, Rb_2SO_4, and Cs_2SO_4. In fact, for a strong binary electrolyte one has: $z_+\tau_+ + z_-\tau_- = 1$ (where both z_- and τ_- are negative), or, equivalently: $t_+ + t_- = 1$, according to whether one adopts the 'signed' of the 'unsigned' definition of transference number [1]. Now, if $\tau_+ \equiv t_+ = 0.5$ (present results), for the 1:2-valent salts it follows that $|\tau_-| = \frac{1}{2}t_- = 0.25$, whereas the equitransference condition for the minimization of liquid junction potentials (see [1–3]) requires $\tau_+ = |\tau_-| = 1/(z_+ + |z_-|) = 0.333$, or in other terms, $t_+ = \frac{1}{2}t_- = 0.333$ and $t_- = 0.667$. Therefore, K_2SO_4, Rb_2SO_4 and Cs_2SO_4 are definitely not appropriate as (unsymmetrical) salt bridges, and analysis of the relevant e.m.f. data is of no further interest (compare with Table 1). The situation of Li_2SO_4 would, instead, appear promising and acceptably conforming to the required equitransference conditions, if one looks to the literature data for the relevant infinite-dilution transference numbers. Actually, the E against $E_{\max}$ correlation is parabolic and leads to $\tau^0_{Li^+} = |\tau^0_{SO_4^{2-}}| = 0.314$. However, upon increasing concentration, $\tau_{Li^+} = |\tau_{SO_4^{2-}}|$ is seen to decrease gradually down to 0.230 at $m_2 = 3\,\mathrm{mol\,kg^{-1}}$ (compare with Table 1 of the preceding paper [1]), which makes Li_2SO_4 useless as a salt bridge. This behaviour is undoubtedly linked with rather high values of the water transference number, $\tau_w^0 = 1.25$, and the primary hydration number, $h = 10$. The non-equitransference here ascertained for the aqueous alkali-metal sulphates makes it rather improbable that equitransference may be found among the other families of aqueous unsymmetrical salts.

Let us now examine in detail the data for CsCl, Table 2, by determining the relevant values of τ_+, τ_w, and the primary hydration number, h, of CsCl, in order to give a critical assessment of the equitransference properties of aqueous CsCl. The procedure of multiple nonlinear regression is the same as described in the preceding paper [1]. To account for the simultaneous dependence of τ_{Cs^+} and τ_w on the CsCl concentration, Stokes's equation [13, 14]:

$$\begin{aligned} t_{Cs^+} \equiv \tau_{Cs^+} &= \frac{\lambda_{Cs^+}}{\Lambda_{CsCl}} \\ &= \frac{[\lambda^0_{Cs^+} - \frac{1}{2}\mathrm{f}(I)]}{[\Lambda^0_{CsCl} - \mathrm{f}(I)]} \\ &= \frac{[t^0_{Cs^+} - \frac{1}{2}]}{[1 - \mathrm{f}(I)/\Lambda^0_{CsCl}]} + \frac{1}{2} \end{aligned} \tag{6}$$

where $\mathrm{f}(I) = B_2 I^{\frac{1}{2}}/(1 + a_0 B I^{\frac{1}{2}})$ with $I = m_2$ and $a_0 = 0.30\,\mathrm{nm}$ [15], and $\Lambda^0_{CsCl} = 153.61\,\Omega^{-1}\mathrm{cm^2\,mol^{-1}}$ [16], has been used to express τ_{Cs^+} in Equation 5. τ_w has, in turn, been expressed by:

$$\tau_w = \tau_w^0 (1 - hm_2M_w) \tag{7}$$

(where τ_w^0 is the limiting value of τ_w, and h is the primary hydration number of CsCl, assumed to be concentration independent), based on the assumption of constancy of the ratio of τ_w to the number of moles of unbound water [17]. By multiple non-linear regression performed through the SAS Statistical Package [18], the three key parameters have been optimized as: $\tau^0_{Cs^+} \equiv t^0_{Cs^+} = 0.5108 \pm 0.0006$, $\tau_w^0 = 0.0080 \pm 0.0008$, and $h = 3.32 \pm 0.17$. Table 2 reports τ_{Cs^+} and τ_w obtained through Equations 6 and 7, as functions of m_2.

The following considerations can be drawn:

(a) Aqueous CsCl obeys equitransference (that is, $\tau_+ = |\tau_-| = -\tau_-$) over the whole concentration range, more closely than any other alkali-metal halide hitherto studied. Thus, it is extremely interesting as a salt bridge, considering also its saturation concentrations: $11.30\,\mathrm{mol\,kg^{-1}}$ at 25° C, 12.15 at 37° C, 12.98 at 50° C, and 15.45 at 90° C [19], which are far higher than those of all the familiar salt bridges hitherto used in electroanalysis, excepting NH_4NO_3 and NH_4I, whose equitransference is, however, inferior to that of CsCl and, at high concentrations, must yet be critically assessed.

(b) Direct determinations of τ_{Cs^+} for CsCl at temperatures higher than 25° C are hindered by the lack of the activity coefficients of CsCl required for the calculation of the $E_{\max}$'s at the various molalities explored. However, it was observed that, with few exceptions, at finite molalities the transference numbers τ_+ and $|\tau_-|$ of the strong binary electrolytes generally become more nearly equal with rising temperature [24, 25]. In fact, this trend can be confirmed for the case of CsCl from the τ_+ results in Table 2 and the infinite-dilution $\tau^0_{Cs^+}$ values in literature [16].

(c) The primary hydration number found, $h_{CsCl} = h_{Cs^+} + h_{Cl^-} = 3.32 \pm 0.17$, is in excellent agreement with the separate ionic values, $h_{Cs^+} = 0$ and $h_{Cl^-} = 3$, as determined by direct methods [20–23], which provides confirmation of the validity of the present treatment.

(d) A close-to-zero (or slightly negative) τ^0_w value, and τ_w values decreasing towards negative values with increasing concentration (as shown in Table 2), are as expected for CsCl, compared, for example, with the $\tau^0_w = 1.25$ value observed for the highly hydrated Li_2SO_4 [1].

4. Conclusions

The results of the present investigation lead to the identification of aqueous CsCl as an outstanding salt bridge both in terms of close equitransference and of very high practicable concentrations. Among its advantageous features one must emphasise the following:

(i) CsCl can be standardized for use at all of the practical concentrations at which the popular KCl salt bridge is currently used, for example, 0.1, 0.16, 1, 1.75, 3.5, 4, and 4.804 mol kg^{-1} (saturated KCl at 25° C), with no inconvenience;

(ii) at the 4.804 mol kg^{-1} level, CsCl is still unsaturated which constitutes a considerable convenience, as crystallization of salt is avoided;

(iii) the CsCl saturation level (11.30 mol kg^{-1} at 25° C) allows minimization of liquid junction potentials even at junctions with sample solutions of much higher ionic strengths than those currently treatable with the saturated KCl salt bridge; and

(iv) for pIon-metric and pH-metric determinations in physiological solutions, the CsCl bridges would be a definitely better choice than the KCl bridges in that the K^+ ions are characteristic components of the physiological solution, and K^+ leakage from KCl bridge to sample solution might introduce significant error.

From the present results it is also clear that any realistic search for new aqueous salt bridges should concentrate on symmetrical 1:1-valent salts CA where $C^+ = K^+, NH_4^+, Rb^+$, or Cs^+ and $A^- = Cl^-, Br^-, I^-$, or NO_3^-, that have τ^0_+, or $|\tau^0_-|$, reasonably approaching the 0.5 value [16]. This constitutes a grid of 16 salts that are either unhydrated (special case of CsI, $h_{CsI} = 0$) or of low h_{CA}, and have either $h_+ = h_-$ (CsI, RbBr, KCl) or a low value of $(h_+ - h_-)$. The critical assessment of the influence of the h and τ_w terms on the effectiveness of a concentrated aqueous salt bridge in minimizing liquid junction potentials (E_L) is still hindered by lack of comparative h and τ_w results and by the physical meaning of h_+ and h_- in the Bates-Staples-Robinson equation [26] leading to the complete expression of the conditions for zeroing E_L (Equations (20) and (26) in the preceding paper [1]). Assuming h to be independent of salt concentration proves functional and does not cause remarkable distortions within the present scheme of treatment. The very complex and demanding treatment worked out lately by Stokes and Robinson [26–28] to describe the decrease of h with increasing concentration of aqueous LiCl in the range from about 10 to 20 mol kg^{-1} [28] is hardly amenable to standardizing applications, and its use is unnecessary in the present context.

What is needed is the characterization or confirmation of the equitransference for as many other salt bridges as possible among the above mentioned grid of 16 special salts, at the highest concentrations, exploiting the convenience and reliability of the method of the homoionic transference cell just described here and in the preceding paper [1]. The recent availability of membrane-based electrodes selective to such ions as NH_4^+ and NO_3^- to which no thermodynamically reversible electrode can be set up, may prove helpful to study the equitransference of the important NH_4NO_3 salt bridge. Extension of application of the present procedure to non-aqueous solvents might prove as successful and gratifying as in pure water, in spite of the additional necessity of prior characterization of appropriate reversible electrodes for the solvents concerned. Such a search is highly desirable and overdue.

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