Transference Numbers of Concentrated Electrolytes and Characterization of Salt Bridges in the Ethanol + Water Solvent Mixtures

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Electromotive force measurements have been made using the transference cells: Ag|AgCl|MCl (m_2)|MCl (m_1)|AgCl|Ag and M(Hg)|MCl (m_1)|MCl (m_2)|M(Hg) (where M = Na, K, and Cs and M(Hg) denotes a flowing M-amalgam electrode) at various molalities $m_2 > m_1$ of MCl salts in ethanol (1) + water (2) with ethanol mass fraction w_1 up to 0.8. The results indicate that the ions in CsCl have approximately equal transference number from pure water up to $w_1 = 0.6$ for ethanol, but at $w_1 = 0.7$ the transference numbers of the ions start to differ. Also, the transference numbers of the ions in KCl in ethanol + water approach 0.5, but at $w_1 > 0.4$, the KCl solubility becomes insufficient for a salt bridge function. NaCl, which is not good as a salt bridge in water, is more useful with increasing ethanol concentrations, and the transference numbers of the ions approach 0.5 at ethanol mass fraction $w_1 > 0.8$.

Introduction

In many types of electrochemical cells it is established practice to insert a salt bridge (*i.e.*, an appropriate concentrated binary salt (Guggenheim, 1930; Covington, 1969; Bates, 1973; Mussini, 1988) whose ions have appproximately equal transference numbers) between sample solution and reference electrode solution for zeroing the diffusion potential (liquid junction potential) arising at the solution junction.

For aqueous solutions there are a number of good salt bridges, see Mussini and co-workers (Mussini *et al.*, 1990; Longhi *et al.*, 1990; Mussini *et al.*, 1993). This research was motivated by the paucity of salt bridges for nonaqueous or water + organic solvent systems.

A key feature of a salt bridge CA is its equitransference (*i.e.*, equal mobilities, $u_C = u_A$, or equal transference numbers, $t_C = t_A = 0.5$, for the cation C^{z+} and the anion A^{z-}). The characterization of a new salt bridge requires a systematic study of transference numbers over a wide range of concentrations in the appropriate solvent S. This is conveniently done by measuring the electromotive forces (emf) of Helmholtz's transference cells of the types:

$$A|CA\ (m_2)|CA\ (m_1)|A \qquad \text{(I)}$$

$$C|CA\ (m_1)|CA\ (m_2)|C \qquad \text{(II)}$$

where $m_2 > m_1$ are CA molalities in solvent S, CA is a simplified notation for $C_{\nu+}^{z+}A_{\nu-}^{z-}$, A and C denote electrodes reversible to the anion A^{z-} and to the cation C^{z+}, respectively, and E_A and E_C the corresponding emfs of cells I and II, respectively; $\nu_C + \nu_A = \nu$ and $\nu_C z_C = \nu_A|z_A|$.

This method requires combining the emfs E_A and/or E_C with E_{MAX} of Helmholtz's double cell (III) without transference:

$$A|CA\ (m_2)|C - C|CA\ (m_1)|A \qquad \text{(III)}$$

or

$$C|CA\ (m_1)|A - A|CA\ (m_2)|C \qquad \text{(III)}$$

For either configuration of cell III, E_{MAX} has one, identical expression, *viz.*

$$E_{MAX} = (\nu k/\nu_C z_C) \ln\{m_2\gamma_2/m_1\gamma_1\} = (\nu k/\nu_A|z_A|) \ln\{m_2\gamma_2/m_1\gamma_1\} \qquad (1)$$

where γ denotes the mean molal activity coefficient of CA at molality m, $k = RT/F$, R = gas constant, F = Faraday's constant, and T = absolute temperature. If E_A, E_C, and E_{MAX} are measured with m_1 = fixed = m_f and m_2 = variable = m, the classical scheme of treatment would lead to the pair of symmetrical equations:

$$dE_A/dE_{MAX} = t_C \quad \text{and} \quad dE_C/dE_{MAX} = t_A \qquad (2)$$

where $t_C + t_A = 1$ and

$$dE_A + dE_C = dE_{MAX} \quad \text{and} \quad E_A + E_C = E_{MAX} \qquad (3)$$

Equation 2 is unfortunately incomplete because it considers only transfer of ions (C^{z+} or A^{z-}) and ignores transfer of solvent S. Mussini *et al.* (Mussini *et al.*, 1990; Longhi *et al.*, 1990), in an extensive study of 1:1 electrolytes in water, showed that t_C in eq 2 is an "apparent" transference number (here denoted as t_C(APP)), and the correct and complete form of eqs 2 is

$$dE_A/dE_{MAX} = t_C(\text{APP}) = t_C - \tau_S M_S m \quad \text{and} \quad dE_C/dE_{MAX} = t_A(\text{APP}) = t_A + \tau_S M_S m \qquad (4)$$

where $\tau_S M_S m$ is the solvent-transfer contribution, M_S is the molar mass of solvent S, and t_C complies with the Stokes–Robinson equation (Stokes, 1954; Robinson and Stokes, 1965a):

$$t_C = [\lambda°_C - {}^1/_2 B_2\sqrt{m}/(1 + a_0B\sqrt{m})]/[\Lambda°_{CA} - B_2\sqrt{m}/(1 + a_0B\sqrt{m})] = [t°_C - 0.5]/\{1 - B_2\sqrt{m}/[(1 + a_0B\sqrt{m})\Lambda°_{CA}]\} + 0.5 \qquad (5)$$

where $t°_C = \lambda°_C/\Lambda°_{CA}$ is the limiting (infinite-dilution) cation transference number, B_2 and B are classical constants of

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the Debye–Hückel–Onsager theory, a_0 is the ion-size parameter, and $\lambda°_C$ and $\Lambda°$ are the limiting molar conductivities of C^- and CA, respectively, in solvent S. The solvent transfer number τ_S (moles of S transferred per Faraday inside cell from negative pole to positive pole) can be expressed (Mussini *et al.*,1990; Longhi *et al.*, 1990) as

$$\tau_S = \tau°_S(1 - hM_Sm) \tag{6}$$

where $\tau°_S$ is the limiting (infinite-dilution) transference number of solvent S and $h = h_C + h_A$ is the primary solvation (hydration) number of CA, which can be estimated by some of the existing independent methods for the determination of the ionic hydration numbers h_C and h_A.

The classical procedure implies that measurements of E_A and E_{MAX} can be related by

$$E_A = \boldsymbol{a}E_{MAX} + \boldsymbol{b}(E_{MAX})^2 + ... \tag{7}$$

and the first derivative

$$dE_A/dE_{MAX} = t_C(APP) = \boldsymbol{a} + 2\boldsymbol{b}E_{MAX} + ... \tag{8}$$

is a function of molality m through E_{MAX} and eq 1; dE_A/dE_{MAX} is (wrongly) equalized to the "true" t_C and (rightly) attributed to the variable molality m of CA. Equation 7, usually truncated at the $(E_{MAX})^2$ term, has two key drawbacks: (*i*) It assumes a rather unrealistic parabolic E_A *vs* E_{MAX} correlation. The present results indicate a straight line at low and intermediate CA molalities which becomes a flat curve at higher molalities, *i.e.*, it really has an oblique asymptote. (*ii*) It cannot be extrapolated to infinite dilution ($m = 0$) because from eq 1 E_{MAX} would become indeterminate. For a few salts the E_A *vs* E_{MAX} plot is a straight line covering the whole molality range: this happens typically with those salts that fulfil the equitransference requirements of salts bridges, namely both $t°_C \approx t°_A \approx 0.5$ at infinite dilution and $t_C \approx t_A \approx 0.5$ at finite concentrations, a feature that is fully justified in terms of the Stokes–Robinson equation (eq 5) (Stokes, 1954; Robinson and Stokes, 1965a).

In the present work we replace eq 7 with the following equation:

$$E_A = \boldsymbol{a}E_{MAX} - \boldsymbol{b}\ exp(\boldsymbol{c}E_{MAX}) \tag{9}$$

From eqs 9 and 4, we have

$$dE_A/eE_{MAX} = t_C(APP) = t_C - \tau_SM_Sm = \boldsymbol{a} - \boldsymbol{bc}\exp(\boldsymbol{c}E_{MAX}) \tag{10}$$

and, from eq 1 for E_{MAX}, we can write

$$dE_A/dE_{MAX} = t_C(APP) = t_C - \tau_SM_Sm = \boldsymbol{a} - Q\,[(m\gamma)_{CA}]^{2k\boldsymbol{c}} \tag{11}$$

where $Q = \boldsymbol{bc}[(m_f\gamma_f)_{CA}]^{-2k\boldsymbol{c}}$ = constant. Extrapolating eq 11 to infinite dilution ($m = 0$, $\gamma = 1$), we have $\tau_SM_Sm = 0$ for the solvent-transfer term, and the limiting slope is given by

$$dE_A/dE_{MAX} = \boldsymbol{a} = t°_C(APP) = t°_C \tag{12}$$

If a rectilinear E_A *vs* E_{MAX} correlation over the whole molality range is observed, eq 7 would become $E_A = \boldsymbol{a}E_{MAX}$ and dE_A/dE_{MAX} would be identical with that from eq 12.

Experimental Section

In cells I, II, and III, the anion-reversible electrodes A are silver/silver chloride electrodes and the cation-reversible electrodes C are flowing M-amalgam electrodes (M = Na, K, and Cs) (Mussini and Pagella, 1971), so that the cell configurations considered were

$$Ag|AgCl|MCl\ (m_2 = m)|MCl\ (m_1 = m_f)|AgCl|Ag \quad (I)$$

$$M(Hg)|MCl\ (m_1 = m_f)|MCl\ (m_2 = m)|M(Hg) \quad (II)$$

$$Ag|AgCl|MCl\ (m_2 = m)|M(Hg){-}M(Hg)|MCl\ (m_1 = m_f)|AgCl|Ag \quad (III)$$

The silver/silver chloride electrodes were prepared according to the bielectrolytic method (Ives and Janz, 1961). Details for the preparation and use of the flowing M-amalgam electrodes, as well as for the potentiometric apparatus and the temperature control design, are given in an earlier paper (Mussini and Pagella, 1971). All emfs were measured at 25 °C. The accuracy of emf measurements was ±0.03 mV and that of temperature control was ±0.05 °C. The MCl solutions in ethanol + water mixed solvents were prepared by mass from redistilled deionized water and the following chemicals: NaCl, Baker, 99.8% purity; KCl, Merck, >99.5%; CsCl, Fluka, >99.5%; ethanol (CH_3CH_2OH), Carlo Erba, 99.99%. The accuracy in the molality m values was better than ±0.015%. Densities of the ethanol + water mixtures were measured by a DMK K40 microdensimeter equipped with a Haake D3 thermostat, and the results (Table 8) are in excellent agreement with the existing literature data (Janz and Tomkins, 1972a; Sankar *et al.*, 1979).

Results and Discussion

Tables 1–3 report the emf E_A of cell I together with the corresponding E_{MAX} results for cell III, as a function of the variable molality $m = m_2$ of the electrolyte MCl ($M^- = Na^-$, K^-, Cs^-) at fixed molality $m_f = m_1$ in the ethanol + water solvent mixtures with various mass fractions w_1 of ethanol at 25 °C. The E_C measurements of cell II have been converted to E_A values through E_{MAX} and eq 3 to provide a single data set. Furthermore, E_{MAX} has not been measured but simply calculated through eq 1 because accurate activity coefficients γ for MCl over the required molality ranges are available from the literature (Mussini *et al.*, 1995; Esteso *et al.*, 1989).

Figure 1 shows the relationship between E_A and E_{MAX} for CsCl and NaCl (KCl behaves similarly to CsCl). For CsCl (straight line $E_A = \boldsymbol{a}E_{MAX}$ covering the whole molality range with $\boldsymbol{a}$ close to 0.5) we used the relationship

$$(dE_A/dE_{MAX})_{CsCl} = \boldsymbol{a} = t°_{Cs}(APP) = t°_{Cs} \tag{13}$$

whereas for NaCl we used eq 9. Optimization of the parameters of eq 9 through a statistical package (SAS, 1985) leads to the $t°_{Na} = \boldsymbol{a}$ results in Table 4, second column. A second approach has been tried: at low NaCl molalities E_A shows a linear relationship with E_{MAX} whose slope (*i.e.*, the limiting slope $\boldsymbol{a}$) gives $t°_{Na} = \boldsymbol{a}$. This avoids the need to consider the rather scattered E_A measurements at the highest molalities. This second set of $t°_{Na}$ values is quoted in Table 4, third column, for comparison. Considering the cumulative uncertainties, the two sets are in substantial agreement.

Table 1. Emfs E_A of the Transference Cell (I) and E_{MAX} of the Double Cell (III) at Various Molalities m of NaCl in Ethanol (1) + Water (2) Solvent Mixtures with Ethanol Mass Fractions w_1 at 25 °C[a]

$w_1 = 0.2$ ($m_f = 0.1$ mol·kg^{-1}; $\gamma_\pm = 0.724$)			$w_1 = 0.4$ ($m_f = 0.1$ mol·kg^{-1}; $\gamma_\pm = 0.658$)			$w_1 = 0.6$ ($m_f = 0.1$ mol·kg^{-1}; $\gamma_\pm = 0.561$)			$w_1 = 0.8$ ($m_f = 0.05$ mol·kg^{-1}; $\gamma_\pm = 0.480$)		
m/(mol·kg^{-1})	E_A/V	E_{MAX}/V	m/(mol·kg^{-1})	E_A/V	E_{MAX}/V	m/(mol·kg^{-1})	E_A/V	E_{MAX}/V	m/(mol·kg^{-1})	E_A/V	E_{MAX}/V
0.01	−0.046 09	−0.108 44	0.02	−0.031 27	−0.072 87	0.025	−0.025 76	−0.059 33	0.01	−0.029 31	−0.066 24
0.01	−0.046 29	−0.108 44	0.02	−0.031 37	−0.072 87	0.025	−0.025 70	−0.059 33	0.01	−0.029 24	−0.066 24
0.03	−0.023 92	−0.055 90	0.03	−0.022 91	−0.054 14	0.05	−0.012 68	−0.029 21	0.02	−0.016 57	−0.037 76
0.03	−0.024 11	−0.055 90	0.03	−0.023 17	−0.054 14	0.05	−0.012 68	−0.029 21	0.02	−0.016 54	−0.037 76
0.05	−0.013 21	−0.031 96	0.05	−0.013 72	−0.030 91	0.07	−0.006 52	−0.014 93	0.03	−0.009 42	−0.021 24
0.05	−0.013 22	−0.031 96	0.05	−0.013 36	−0.030 91	0.07	−0.006 41	−0.014 93	0.03	−0.009 48	−0.021 24
0.07	−0.006 90	−0.016 38	0.07	−0.006 72	−0.015 83	0.3	0.017 96	0.045 37	0.06	0.003 16	0.007 69
0.07	−0.006 80	−0.016 38	0.07	−0.006 71	−0.015 83	0.3	0.018 01	0.045 37	0.06	0.003 16	0.007 69
0.2	0.013 21	0.031 56	0.2	0.012 69	0.030 42	0.5	0.026 77	0.066 72	0.08	0.007 94	0.019 56
0.2	0.013 20	0.031 56	0.2	0.012 73	0.030 42	0.5	0.026 76	0.066 72	0.08	0.007 96	0.019 56
0.3	0.020 89	0.050 02	0.3	0.020 20	0.048 13	0.7	0.032 66	0.081 13	0.1	0.011 85	0.027 77
0.3	0.020 88	0.050 02	0.3	0.020 20	0.048 13	0.7	0.032 66	0.081 13	0.1	0.011 87	0.027 77
0.5	0.030 12	0.073 46	0.5	0.029 29	0.070 60	0.15	0.007 31*	0.016 79	0.06	0.003 36*	0.007 69
0.5	0.030 13	0.073 46	0.5	0.029 09	0.070 60	0.3	0.019 19*	0.045 37	0.06	0.003 40*	0.007 69
0.7	0.036 45	0.089 20	0.8	0.037 71	0.091 70	0.3	0.018 77*	0.045 37	0.08	0.008 42*	0.019 56
0.7	0.036 46	0.089 20	0.8	0.037 67	0.091 70	1	0.040 20*	0.096 80	0.1	0.011 96*	0.027 77
1	0.043 15	0.106 36	1	0.041 83	0.101 97						
1	0.043 26	0.106 36	1	0.041 83	0.101 97						
1.3	0.048 27	0.119 49	1.2	0.045 15	0.110 54						
1.3	0.048 28	0.119 49	1.2	0.045 20	0.110 54						
1.6	0.052 27	0.130 30	1.5	0.049 56	0.121 31						
1.6	0.052 26	0.130 30	1.5	0.049 55	0.121 31						
2	0.057 10	0.142 49	0.2	0.013 52*	0.030 42						
2	0.057 32	0.142 49	0.2	0.013 52*	0.030 42						
0.5	0.030 76*	0.073 46	0.3	0.019 13*	0.048 13						
0.5	0.030 76*	0.073 46	0.5	0.030 25*	0.070 60						
0.7	0.036 57*	0.089 20	0.5	0.029 75*	0.070 60						
1	0.043 55*	0.106 36	0.8	0.038 41*	0.091 70						
1.3	0.048 46*	0.119 49	1	0.042 70*	0.101 97						
1.6	0.053 34*	0.130 30	1.2	0.046 29*	0.11054						
2	0.057 79*	0.142 49	1.5	0.050 66*	0.12131						

[a] Starred values (*) are emfs E_C of the transference cell (II) converted to E_A through E_{MAX} using eq 3.

Table 2. Emfs E_A of the Transference Cell (I) and E_{MAX} of the Double Cell (III) at Various Molalities m of KCl in Ethanol (1) + Water (2) Solvent Mixtures with Ethanol Mass Fractions w_1 at 25 °C[a]

$w_1 = 0.2$ ($m_f = 0.1$ mol·kg^{-1}; $\gamma_\pm = 0.713$)			$w_1 = 0.4$ ($m_f = 0.1$ mol·kg^{-1}; $\gamma_\pm = 0.648$)		
m/(mol·kg^{-1})	E_A/V	E_{MAX}/V	m/(mol·kg^{-1})	E_A/V	E_{MAX}/V
0.02	−0.038 05	−0.074 52	0.02	−0.035 10	−0.072 27
0.02	−0.038 40	−0.074 52	0.03	−0.026 76	−0.053 61
0.03	−0.028 26	−0.055 39	0.03	−0.026 89	−0.053 61
0.03	−0.028 52	−0.055 39	0.05	−0.015 07	−0.030 53
0.05	−0.016 14	−0.031 63	0.05	−0.015 28	−0.030 53
0.05	−0.016 20	−0.031 63	0.07	−0.007 88	−0.015 60
0.07	−0.008 37	−0.016 19	0.07	−0.008 02	−0.015 60
0.07	−0.008 39	−0.016 19	0.2	0.014 76	0.029 65
0.2	0.015 82	0.030 97	0.2	0.014 82	0.029 65
0.2	0.016 10	0.030 97	0.3	0.022 71	0.046 63
0.3	0.025 10	0.048 83	0.3	0.022 94	0.046 63
0.3	0.025 13	0.048 83	0.2	0.014 39*	0.029 65
0.2	0.015 79*	0.030 97	0.2	0.013 99*	0.029 65
0.3	0.025 38*	0.048 83	0.2	0.013 79*	0.029 65
0.5	0.037 42*	0.071 17	0.3	0.023 38*	0.046 63
0.8	0.047 35*	0.091 65	0.4	0.029 32*	0.058 52
1.4	0.059 26*	0.116 07	0.4	0.029 62*	0.058 52
2	0.066 64*	0.131 74	0.6	0.037 06*	0.075 06
2	0.067 04*	0.131 74	0.8	0.042 84*	0.086 64
			0.8	0.042 86*	0.086 64
			1	0.047 66*	0.095 51
			1.2	0.050 99*	0.102 69
			1.2	0.050 84*	0.102 69

[a] Starred values (*) are emfs E_C of the transference cell (II) converted to E_A through E_{MAX} using eq 3.

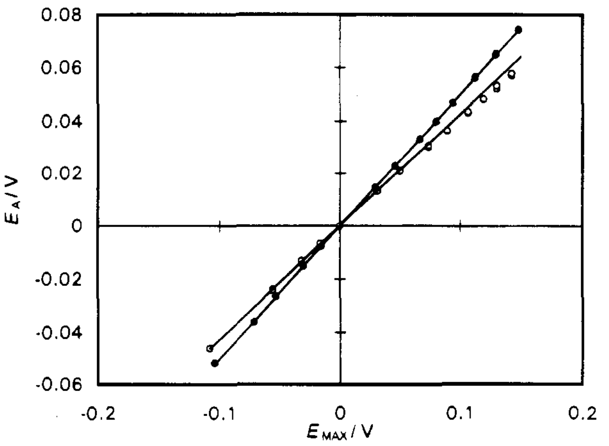

Figure 1. Relationship between E_A and E_{MAX} in ethanol + water solvent mixtures at 25 °C: (○) linear (CsCl in 40 mass % ethanol) and (●) asymptotic (NaCl in 20 mass % ethanol).

For KCl and CsCl, $t°_C$ is close to 0.5 (Table 4) with a perceptible maximum at about 20 mass % ethanol, probably resulting from the complex overlapping effects of relative permittivities, viscosities, and primary solvation numbers. [A similar maximum was observed also by Harned and Dreby (Harned and Dreby, 1939) for $t°_H$ of hydrochloric acid in 1,4-dioxane + water mixtures.] Earlier $t°_K$ values for KCl in ethanol + water (Esteso and Grandoso, 1980; Fratiello and Kay, 1974; Erdey-Gruz and Majthenyi, 1959) are remarkably scattered. The present $t°_K$ value in 20 mass % ethanol substantiates the moving-boundary results by Esteso and Grandoso and by Fratiello and Kay, considering the cumulative uncertainties; in 40 mass % ethanol, the present $t°_K$ value confirms Erdey-Gruz and Majthenyi's results rather than Fratiello and Kay's.

For NaCl, $t°_{Na}$ first increases steeply from pure water to 20 mass % ethanol and then less pronouncedly and almost linearly up to 80 mass % ethanol. This unusual result has prompted an inspection of the limiting ionic mobilities $u° = \lambda°/F = t°\Lambda°/F$ and of Stokes' law ionic radii $r_{St} = 0.82/\lambda°\eta$, where η is the solvent viscosity. Two facts emerge: (i) the mobility $u°_{Na}$ of the Na^- ion is 20–30% lower than those of the other three ions (K^-, Cs^-, Cl^-) which are almost identical over the whole range of solvent composition and (ii) Stokes' radius $(r_{St})_{Na}$ is always greater than the corresponding crystallographic radius $(r_{cr})_{Na}$, whereas for K^-, Cs^-, and Cl^- the contrary is true. This implies that Na^- has a big primary solvation sheath and its mechanism of motion in ethanol + water mixtures is that of viscous motion, unlike the other three ions. Therefore, NaCl should, in terms of transference parameters, behave rather differently from KCl and CsCl, as Table 4 confirms.

From the limiting cationic transference numbers $t°_C$, the t_C values at finite molalities can be calculated from eq 5 using the $\Lambda°_{CA}$ values from the literature. These $\Lambda°_{CA}$ values as a function of solvent composition are rather sparse (Landolt-Bornstein, 1960; Janz and Tomkins, 1972) and have been submitted to regression to obtain the following smoothing polynomials, useful for interpolation:

$$\Lambda°_{NaCl}/(\Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}) = 125.71 - 414.52w_1 + 833.27(w_1)^2 - 788.29(w_1)^3 + 286.12(w_1)^4 \quad (14a)$$

$$\Lambda°_{KCl}/(\Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}) = 149.84 - 483.61w_1 + 889.75(w_1)^2 - 772.61(w_1)^3 + 262.34(w_1)^4 \quad (14b)$$

$$\Lambda°_{CsCl}/(\Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}) = 153.64 - 465.79w_1 + 794.84(w_1)^2 - 652.61(w_1)^3 + 218.29(w_1)^4 \quad (14c)$$

where w_1 is the mass fraction of ethanol in the ethanol (1) + water (2) solvent mixture. The ancillary quantities used for the calculation of the B and B_2 constants in eq 5, together with the relevant ion-size parameters a_0 (Mussini *et al.*, 1995; Esteso *et al.*, 1989), are collected in Table 8. An inspection of the sensitivity of the $t°_C$ calculation to the a_0 values used focuses the following: (i) If $t°_C = 0.5$ exactly (ideal salt bridge), eq 5 shows that, at any salt concentration, t_C is unaffected by the a_0 value and it coincides with $t°_C = 0.5$. (ii) If $t°_C \approx 0.505$ (cases of CsCl and KCl) a ±0.05 nm change in a_0 (about 15–30%) would affect t_C by only ∓0.0001, 0.0002, 0.0004, 0.0006, and 0.0007 at the molalities of 0.1, 1, 2, 4, and 7 mol·kg^{-1}, respectively, at the

Table 3. Emfs E_A of the Transference Cell (I) and E_{MAX} of the Double Cell (III) at Various Molalities m of CsCl in Ethanol (1) + Water (2) Solvent Mixtures with Ethanol Mass Fractions w_1 at 25 °C[a]

$w_1 = 0.2$ ($m_f = 0.1$ mol·kg^{-1}; $\gamma_f = 0.700$)			$w_1 = 0.4$ ($m_f = 0.1$ mol·kg^{-1}; $\gamma_f = 0.637$)			$w_1 = 0.6$ ($m_f = 0.1$ mol·kg^{-1}; $\gamma_f = 0.541$)			$w_1 = 0.7$ ($m_f = 0.1$ mol·kg^{-1}; $\gamma_f = 0.488$)		
m/(mol·kg^{-1})	E_A/V	E_{MAX}/V	m/(mol·kg^{-1})	E_A/V	E_{MAX}/V	m/(mol·kg^{-1})	E_A/V	E_{MAX}/V	m/(mol·kg^{-1})	E_A/V	E_{MAX}/V
0.01	−0.055 15	−0.10691	0.01	−0.051 89	−0.104 08	0.01	−0.047 64	−0.099 02	0.01	−0.044 73	−0.096 04
0.02	−0.038 33	−0.07381	0.01	−0.051 80	−0.104 08	0.01	−0.047 37	−0.099 02	0.01	−0.044 81	−0.096 04
0.02	−0.038 21	−0.07381	0.02	−0.036 17	−0.071 65	0.02	−0.032 62	−0.067 75	0.02	−0.030 95	−0.065 49
0.03	−0.027 95	−0.05478	0.02	−0.036 13	−0.071 65	0.02	−0.032 63	−0.067 75	0.02	−0.030 65	−0.065 49
0.03	−0.028 33	−0.05478	0.03	−0.026 49	−0.053 09	0.03	−0.024 01	−0.050 02	0.03	−0.022 20	−0.048 24
0.05	−0.016 58	−0.03121	0.03	−0.026 45	−0.053 09	0.03	−0.024 02	−0.050 02	0.05	−0.012 64	−0.027 22
0.05	−0.016 70	−0.03121	0.05	−0.015 20	−0.030 19	0.05	−0.013 48	−0.028 30	0.05	−0.012 61	−0.027 22
0.07	−0.008 88	−0.01595	0.05	−0.015 22	−0.030 19	0.05	−0.013 40	−0.028 30	0.07	−0.006 14	−0.013 82
0.07	−0.008 83	−0.01595	0.07	−0.007 74	−0.015 40	0.07	−0.007 10	−0.014 40	0.07	−0.006 38	−0.013 82
0.2	0.015 57	0.03033	0.07	−0.007 76	−0.015 40	0.07	−0.007 05	−0.014 40	0.2	0.011 66	0.025 68
0.2	0.015 46	0.03033	0.2	0.014 58	0.029 18	0.2	0.012 90	0.027 01	0.2	0.011 71	0.025 68
0.3	0.023 99	0.04768	0.2	0.014 59	0.029 18	0.2	0.012 94	0.027 01	0.3	0.020 56	0.039 97
0.3	0.023 95	0.04768	0.3	0.022 90	0.045 84	0.3	0.020 50	0.042 27	0.2	0.011 75*	0.025 68
0.2	0.015 18*	0.03033	0.3	0.022 89	0.045 84	0.3	0.020 37	0.042 27	0.2	0.011 69*	0.025 68
0.3	0.023 78*	0.04768	0.2	0.014 58*	0.029 18	0.2	0.013 71*	0.027 01	0.3	0.017 91*	0.039 97
0.3	0.023 83*	0.04768	0.2	0.014 58*	0.029 18	0.3	0.021 73*	0.042 27	0.3	0.019 03*	0.039 97
0.6	0.038 34*	0.07682	0.3	0.022 91*	0.045 84	0.3	0.021 33*	0.042 27	0.3	0.018 93*	0.039 97
1	0.048 82*	0.09796	0.3	0.022 94*	0.045 84	0.5	0.030 38*	0.061 03	0.4	0.023 97*	0.049 76
1.6	0.058 67*	0.11767	0.5	0.033 22*	0.066 46	0.7	0.036 42*	0.073 14	0.4	0.023 91*	0.049 76
2.5	0.068 34*	0.13682	0.5	0.033 25*	0.066 46	1	0.042 61*	0.085 77	0.4	0.023 76*	0.049 76
5	0.084 27*	0.16757	0.7	0.039 95*	0.079 86	1.3	0.047 53*	0.094 92	0.5	0.027 14*	0.057 12
7	0.091 48*	0.18308	0.7	0.039 97*	0.079 86	1.6	0.049 57*	0.102 08	0.5	0.027 11*	0.057 12
			1	0.046 95*	0.093 94	2	0.053 61*	0.109 66	0.5	0.027 09*	0.057 12
			1	0.047 01*	0.093 94				0.6	0.029 91*	0.062 97
			1.6	0.056 27*	0.112 34				0.6	0.029 90*	0.062 97
			1.6	0.056 46*	0.112 34				0.6	0.029 91*	0.062 97
			2.5	0.064 91*	0.129 63				0.8	0.034 10*	0.071 84
			2.5	0.065 28*	0.129 63				0.8	0.033 88*	0.071 84
			4	0.074 10*	0.147 64				0.8	0.033 90*	0.071 84
			4	0.074 36*	0.147 64				1	0.036 40*	0.078 35
									1	0.036 40*	0.078 35
									1	0.036 33*	0.078 35

[a] Starred values (*) are emfs E_C of the transference cell (II) converted to E_A through E_{MAX} using eq 3.

Table 4. Infinite-Diluition Cation Transference Numbers $t°$ at 25 °C for NaCl, KCl, and CsCl in Ethanol (1) + Water (2) Mixed Solvents at Various Ethanol Mass Fractions w_1 with Corresponding Standard Errors

w_1	$t°(Na^+)$		$t°(K^+)$	$t°(Cs^+)$
0[a]	0.3962		0.4891	0.5018
0.2	0.4241 ± 0.0016[b]	0.4267 ± 0.0011[c]	0.5118 ± 0.0012	0.5040 ± 0.0017
0.4	0.4276 ± 0.0029[b]	0.4283 ± 0.0013[c]	0.4954 ± 0.0013	0.5013 ± 0.0004
0.6	0.4257 ± 0.0054[b]	0.4338 ± 0.0004[c]	–	0.4884 ± 0.0019
0.7	–	–	–	0.4702 ± 0.0015
0.8	0.4407 ± 0.0018[b]	0.4417 ± 0.0009[c]	–	–

[a] From Robinson and Stokes, 1965b. [b] From regression along eq 9. [c] From the limiting ($m \to 0$) slope dE_A/dE_{MAX}.

Table 5. Values at 25 °C of the Cation Transference Numbers t_{Na} (Compared with the "Apparent" Transference Numbers $t_{Na}(APP) = dE_A/dE_{MAX}$) for NaCl at Various Molalities m in Ethanol (1) + Water (2) Mixtures with Ethanol Mass Fractions w_1

$w_1 = 0.2$			$w_1 = 0.4$			$w_1 = 0.6$			$w_1 = 0.8$		
m_{NaCl}/(mol·kg^{-1})	t_{Na}	$t_{Na}(APP)$	m_{NaCl}/(mol·kg^{-1})	t_{Na}	$t_{Na}(APP)$	m_{NaCl}/(mol·kg^{-1})	t_{Na}	$t_{Na}(APP)$	m_{NaCl}/(mol·kg^{-1})	t_{Na}	$t_{Na}(APP)$
0[a]	0.4241	0.4241	0[a]	0.4276	0.4276	0[a]	0.4257	0.4257	0[a]	0.4407	0.4407
0.01	0.4210	0.4236	0.02	0.4228	0.4269	0.025	0.4184	0.4229	0.01	0.4347	0.4403
0.03	0.4189	0.4227	0.03	0.4218	0.4266	0.05	0.4159	0.4214	0.02	0.4324	0.4394
0.05	0.4177	0.4219	0.05	0.4204	0.4259	0.07	0.4144	0.4204	0.03	0.4307	0.4382
0.07	0.4167	0.4211	0.07	0.4193	0.4253	0.1	0.4126	0.4191	0.05	0.4380	0.4250
0.1	0.4156	0.4200	0.1	0.4181	0.4243	0.15	0.4104	0.4173	0.06	0.4270	0.4330
0.2	0.4130	0.4166	0.2	0.4152	0.4213	0.2	0.4086	0.4157	0.08	0.4251	0.4284
0.3	0.4113	0.4134	0.3	0.4133	0.4183	0.3	0.4060	0.4130	0.1	0.4235	0.4238
0.5	0.4090	0.4073	0.5	0.4106	0.4125	0.4	0.4039	0.4106			
0.7	0.4074	0.4014	0.8	0.4081	0.4038	0.5	0.4023	0.4084			
1	0.4056	0.3926	1	0.4068	0.3979	0.6	0.4009	0.4063			
1.3	0.4043	0.3835	1.2	0.4058	0.3918	0.7	0.3997	0.4043			
1.6	0.4033	0.3742	1.5	0.4045	0.3825	0.8	0.3987	0.4024			
2	0.4022	0.3610				1	0.3969	0.3989			

[a] Infinite dilution.

Table 6. Values at 25 °C of the Cation Transference Numbers t_K (Compared with the "Apparent" Transference Numbers $t_K(APP) = dE_A/dE_{MAX}$) for KCl at Various Molalities m in Ethanol (1) + Water (2) Mixtures with Ethanol Mass Fractions w_1

$w_1 = 0.2$ ($t_K(APP) = 0.5118$)		$w_1 = 0.4$ ($t_K(APP) = 0.4954$)		$w_1 = 0.2$ ($t_K(APP) = 0.5118$)		$w_1 = 0.4$ ($t_K(APP) = 0.4954$)	
m_{KCl}/(mol·kg^{-1})	t_K	m_{KCl}/(mol·kg^{-1})	t_K	m_{KCl}/(mol·kg^{-1})	t_K	m_{KCl}/(mol·kg^{-1})	t_K
0[a]	0.5118	0[a]	0.4954	0.3	0.5134	0.3	0.4946
0.02	0.5123	0.02	0.4951	0.5	0.5137	0.4	0.4945
0.03	0.5124	0.03	0.4951	0.8	0.5140	0.6	0.4944
0.05	0.5126	0.05	0.4950	1.4	0.5144	0.8	0.4943
0.07	0.5127	0.07	0.4949	2	0.5146	1	0.4943
0.1	0.5129	0.1	0.4949			1.2	0.4942
0.2	0.5132	0.2	0.4947				

[a] Infinite dilution.

Table 7. Values at 25 °C of the Cation Transference Numbers t_{Cs} (Compared with the "Apparent" Transference Numbers $t_{Cs}(APP) = dE_A/dE_{MAX}$) for CsCl at Various Molalities m in Ethanol (1) + Water (2) Mixtures with Ethanol Mass Fractions w_1

$w_1 = 0.2$ ($t_{Cs}(APP) = 0.5040$)		$w_1 = 0.4$ ($t_{Cs}(APP) = 0.5013$)		$w_1 = 0.6$ ($t_{Cs}(APP) = 0.4884$)		$w_1 = 0.7$ ($t_{Cs}(APP) = 0.4702$)	
m_{CsCl}/(mol·kg^{-1})	t_{Cs}	m_{CsCl}/(mol·kg^{-1})	t_{Cs}	m_{CsCl}/(mol·kg^{-1})	t_{Cs}	m_{CsCl}/(mol·kg^{-1})	t_{Cs}
0[a]	0.5040	0[a]	0.5013	0[a]	0.4884	0[a]	0.4702
0.01	0.5041	0.01	0.5013	0.01	0.4877	0.01	0.4680
0.02	0.5042	0.02	0.5014	0.02	0.4874	0.02	0.4672
0.03	0.5042	0.03	0.5014	0.03	0.4872	0.03	0.4666
0.05	0.5043	0.05	0.5014	0.05	0.4869	0.05	0.4657
0.07	0.5043	0.07	0.5014	0.07	0.4867	0.07	0.4650
0.1	0.5044	0.1	0.5014	0.1	0.4864	0.1	0.4641
0.2	0.5045	0.2	0.5015	0.2	0.4857	0.2	0.4622
0.3	0.5046	0.3	0.5015	0.3	0.4853	0.3	0.4609
0.6	0.5048	0.5	0.5016	0.5	0.4847	0.4	0.4599
1	0.5049	0.7	0.5016	0.7	0.4842	0.5	0.4591
1.6	0.5050	1	0.5016	1	0.4837	0.6	0.4584
2.5	0.5052	1.6	0.5017	1.3	0.4833	0.8	0.4573
5	0.5054	2.5	0.5017	1.6	0.4830	1	0.4564
7	0.5055	4	0.5018	2	0.4827		

[a] Infinite dilution.

highest w_1 investigated. (iii) If $t°_C \approx 0.425$ (case of NaCl) such ±0.05 nm change in a_0 would affect t_C by about ±0.001, 0.007, and 0.010 at the molalities of 0.1, 1, and 2 mol·kg^{-1}, respectively, at the highest w_1 studied.

Table 8. Relative Permittivities (ϵ), Viscosities (η), and Densities (ϱ) at 25 °C of Ethanol (1) + Water (2) Solvent Mixtures at Ethanol Mass Fractions w_1, Used for Calculation of B and B_2 Constants, Together with Ion-Size Parameters a_0 for NaCl, KCl, and CsCl, Used in Eq 5

w_1	ϵ^a	$\eta/(\mathrm{Pa{\cdot}s})^b$	$\varrho/(\mathrm{kg{\cdot}dm^{-3}})^c$	$a_0(\mathrm{NaCl})/\mathrm{nm}^d$	$a_0(\mathrm{KCl})/\mathrm{nm}^e$	$a_0(\mathrm{CsCl})/\mathrm{nm}^e$
0.2	66.4	0.0001 82	0.9664	0.37	0.351	0.276
0.4	55.0	0.0002 35	0.9315	0.36	0.357	0.304
0.6	43.4	0.0002 23	0.8871	0.36	–	0.299
0.7	38.0	0.0002 02	0.8636	–	–	0.334
0.8	32.8	0.0001 75	0.8392	0.34	–	–

[a] Interpolated from Sankar *et al.*,1979, and Janz and Tomkins, 1972a. [b] From Janz and Tomkins, 1972b. [c] Present work. [d] From Esteso *et al.*, 1989. [e] From Mussini *et al.*, 1995.

The t_C results are quoted together with the apparent transference numbers t_C(APP) in Tables 5, 6, and 7 for NaCl, KCl, and CsCl, respectively. The solvent transfer contribution $\tau_S M_S m = t_C - t_C(\mathrm{APP})$, as expected from eq 5, is small for KCl and CsCl whereas it is significant for NaCl at low mass fractions of ethanol (where t°_{Na} is considerably lower than 0.5) but small for NaCl at highest mass fractions of ethanol (where t°_{Na} tends to approach the t°_{Cs} value beyond $w_1 = 0.8$). The present purpose is to characterize new salt bridges, so no attempt has been made to evaluate the solvent transfer contribution $\tau_S M_S m$ by direct independent methods, because it would involve determination of distinct transference numbers for ethanol (τ_E) and for water (τ_W) as well as distinct hydration numbers (h_W) and ethanolation numbers (h_E).

The following conclusions can be made:

(1) In ethanol + water mixed solvents, CsCl remains as a quasi-ideal salt bridge, but at ethanol mass fractions higher than 0.6, it tends to loose its quasi-ideal salt bridge character.

(2) KCl shows better behavior in ethanol + water than in pure water, becoming a quasi-ideal salt bridge, but its applicability is inhibited by its low solubility, which makes it inadvisable for studies beyond $w_1 = 0.4$ of ethanol.

(3) NaCl, which in pure water has poor salt bridge characteristics, improves markedly its behavior in ethanol + water to having good salt bridge properties at ethanol mass fraction $w_1 = 0.8$. Above this ethanol concentration, NaCl is likely to become even more equitransferent, but its solubility is a limiting factor.

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