Transference Numbers of Alkali Chlorides and Characterization of Salt Bridges for Use in Methanol + Water Mixed Solvents

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Electromotive force measurements at 25 °C of the transference cells Ag|AgCl|MeCl (m_2)|MeCl (m_1)|AgCl|Ag and Me_xHg_{1-x}|MeCl (m_1)|MeCl (m_2)|Me_xHg_{1-x} (where Me = Li, Na, K, and Rb and Me_xHg_{1-x} denotes a flowing Me-amalgam electrode at Me mole fraction x) have been made at various molalities $m_2 > m_1$ (with m_1 fixed and m_2 varied) in methanol + water solvent mixtures with methanol mass fractions w_M up to 0.8. Supplementary emf measurements have been made of the cell Pt|Li_xHg_{1-x}|LiCl (m_1)|AgCl|Ag|Pt to obtain the required activity coefficients for LiCl at methanol mass fractions $w_M = 0.2$. The general trend of the ionic transference numbers of each MeCl is a $t°_{Me^+}$ increase with w_M, which is much more pronounced for those Me^+'s whose primary hydration sheaths are bigger (namely, Li^+ and Na^+). In particular, KCl becomes exactly equitransferent ($t°_{K^+} = t°_{Cl^-} = 0.5$, i.e. an ideal salt bridge) at $w_M \approx 0.1$, but at $w_M > 0.6$ the KCl solubility becomes insufficient for a salt bridge function. The same drawback occurs also for RbCl, which is known to be the most closely equitransferent salt in water ($t°_{Rb^+} = 0.5007$). NaCl, which is quite unproposable as a salt bridge in water, may be useful at high methanol concentrations, as its ionic transference numbers would approach 0.5 at $w_M \geq 0.8$.

Introduction

In the domain of direct-potentiometry electroanalysis (e.g., pH and pIon measurements) the indispensable practice of inserting a concentrated equitransferent salt bridge between the sample solution and the reference electrode solution to minimize the intervening liquid junction potentials in the operational cell was earlier motivated and discussed in detail (Guggenheim, 1930; Ives and Janz, 1961; Covington, 1969; Bockris and Reddy, 1970; Bates, 1973; Mussini, 1988). In that context, choosing the appropriate salt bridge is important because the residual liquid junction potential gives the major (and hardly assessable) contribution to the total uncertainty in pH and pIon measurements. For such measurements to be reliable, it is well-known that the following four basic conditions must be complied with when measuring the emf's of the operational cell on the sample solution and on the standard reference solution: same temperature, same electrode pair, same salt bridge, and *same solvent*. For the case of working in purely aqueous solutions, a wealth of salt bridges (all of them definitely superior to the popular KCl) have been recently characterized (Mussini et al., 1990b; Mussini et al., 1993; Buizza et al., 1996) and are available for use, CsCl and RbCl being those that most closely approach the behavior of an ideal salt bridge.

Instead, the current availability of salt bridges for use in nonaqueous or aqueous−organic solvents (Spiro, 1971; Spiro 1986) can be only euphemistically defined as very meager, and badly contrasts with the rather satisfactory availability of standards for pH measurements in such media (Mussini et al., 1985; Rondinini et al., 1987a; Rondinini et al., 1987b; Mussini et.al., 1997). Using aqueous salt bridges in contact with nonaqueous or aqueous−organic sample solutions in the operational cell is an unfortunately frequent and depreciable practice, which would mostly lead to meaningless results, due to the occurrence of intersolvent liquid junction potentials (Rondinini et al., 1978). The present work is part of a systematic experimental study in these laboratories with the object of characterizing salt bridges for use in aqueous−organic solvent mixtures, by studying the ionic transference numbers of alkali chlorides in ethanol + water (Mussini et al., 1995), ethylene glycol + water, and 1,4-dioxane + water mixtures (Ceccattini et al., 1998), due attention being given to the solvent-transfer parameters. The results show that alkali chlorides in the above mixed solvent systems significantly change their behavior with respect to that known in water: in particular, NaCl in 80 mass % ethanol and in 60 mass % acetonitrile becomes almost as equitransferent as KCl in water, thus featuring a discrete salt bridge. Similarly, an unsymmetrical valence salt, Li_2SO_4, has been shown to behave as a good salt bridge in certain acetonitrile + water mixtures (Faverio et al., 1998).

The methodology adopted here is that of the emf's of Helmholtz's transference cells, which lends itself best to obtaining accurate data over extended molality ranges of the electrolyte concerned in a variety of solvent mixtures S (Spiro, 1971; Spiro, 1986). The cells in question are

$$\mathrm{Ag|AgCl|MeCl}\ (m_{\mathrm{var}})\mathrm{|MeCl}\ (m_{\mathrm{fix}})\mathrm{|AgCl|Ag} \qquad \mathrm{(I)}$$

$$\mathrm{Me(Hg)|MeCl}\ (m_{\mathrm{fix}})\mathrm{|MeCl}\ (m_{\mathrm{var}})\mathrm{|Me(Hg)} \qquad \mathrm{(II)}$$

whose terminal electrode pairs are, respectively, reversible to the anion (and produce the emf E_A) and to the cation (and produce the emf E_C); Me = Li, Na, K, and Rb is the metal in dilute amalgam (denoted as Me(Hg)), and the MeCl molality m_{fix} is fixed, whereas m_{var} is varied within the required molality range. The purpose of this work is

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Table 1. emf's E_A of the Transference Cell Ag|AgCl|LiCl (m_{Var})|LiCl (m_{fix})|AgCl|Ag, at 25 °C, as a Function of the Variable Molality m_{var} of LiCl in methanol + water Mixed Solvents of Methanol Mass Fraction w_M with Fixed m_{fix} = 0.1 mol·kg^{-1}, Together with the Corresponding E_{MAX} Values (Eq 4)

m_{var}/(mol·kg^{-1})	γ[a]	E_{MAX}/V	E_A/V	m_{var}/(mol·kg^{-1})	γ[a]	E_{MAX}/V	E_A[b]/V
				$w_M = 0.1$			
0.00200	0.948	−0.190 60	−0.059 74	0.0300	0.841	−0.057 60	−0.017 00
0.00500	0.922	−0.144 95	−0.044 50	0.0500	0.817	−0.032 84	−0.009 70
0.00500	0.922	−0.144 95	−0.045 18	0.0700	0.794	−0.017 02	−0.005 25
0.00700	0.910	−0.128 33	−0.040 175	0.1000	0.774	0	0
0.00700	0.910	−0.128 33	−0.039 425	0.2000	0.737	0.033 10	0.010 20
0.0100	0.897	−0.110 74	−0.033 87	0.5000	0.719	0.078 91	0.023 90
0.0100	0.897	−0.110 74	−0.033 61	0.7000	0.724	0.096 56	0.029 10
0.0150	0.878	−0.091 01	−0.027 40	1.0000	0.750	0.116 70	0.035 60
0.0200	0.865	−0.076 99	−0.022 475	2.0000	0.882	0.160 65	0.048 41
				$w_M = 0.2$			
0.00200	0.944	−0.189 19	−0.063 10	0.3002	0.694	0.052 53	0.016 84
0.00532	0.914	−0.140 63	−0.046 29	0.3002	0.694	0.052 53	0.017 43*
0.00748	0.900	−0.123 88	−0.041 32	0.5283	0.685	0.080 87	0.027 075
0.01063	0.885	−0.106 69	−0.035 88	0.5283	0.685	0.080 87	0.026 64*
0.02112	0.850	−0.073 49	−0.024 51	1.9994	0.870	0.161 57	0.048 98
0.05286	0.794	−0.02983	−0.010 50	1.9994	0.870	0.16157	0.049 91*
0.05286	0.794	−0.029 83	−0.011 24*	2.9990	1.112	0.195 01	0.0570 73
0.07385	0.772	−0.014 07	−0.005 36	2.9990	1.112	0.195 01	0.057 88*
0.07385	0.772	−0.014 07	−0.004 44*	5.0048	1.947	0.250 09	0.070 74
0.1000	0.753	0	0	5.0048	1.947	0.250 09	0.070 62*
0.1055	0.749	0.002 71	0.000 28	7.0010	3.592	0.298 81	0.081 71
0.1055	0.749	0.002 71	0.001 35*	7.0010	3.592	0.298 81	0.079 39*
0.2111	0.709	0.035 52	0.010 31	8.9990	6.919	0.345 40	0.090 02
0.2111	0.709	0.035 52	0.011 22*	8.9990	6.919	0.345 40	0.086 93*

[a] Mean molal activity coefficients γ of LiCl taken from the literature (Harned, 1962; Sala, 1999). [b] The E_A values marked * were obtained as $E_A = E_{MAX} - E_C$ (eq 3) from the measured emf's E_C of the transference cell Pt|Li$_x$Hg$_{1-x}$|LiCl (m_{fix})|LiCl (m_{var})|Li$_x$Hg$_{1-x}$|Pt.

Table 2. emf's E_A of the Transference Cell Ag|AgCl|NaCl (m_{Var})|NaCl (m_{Fix})|AgCl|Ag, at 25 °C, as a Function of the Variable Molality m_{var}, in Methanol + Water) Mixed Solvents of Methanol Mass Fractions w_M, with Corresponding E_{MAX} Values (Eq 4)

	0.2			0.4			0.6			0.8		
m_{var}/(mol·kg^{-1})	γ[a]	E_{MAX}/V	E_A[b]/V	γ[a]	E_{MAX}/V	E_A[b]/V	γ[a]	E_{MAX}/V	E_A[b]/V	γ[a]	E_{MAX}/V	E_A[b]/V
0.002	0.942	−0.187 64	−0.077 87	0.930	−0.185 68	−0.079 50	0.912	−0.180 52	−0.080 06	0.882	−0.173 17	−0.080 76
0.005	0.913	−0.142 16	−0.058 95	0.896	−0.140 51	−0.060 27	0.868	−0.135 98	−0.060 30	0.824	−0.129 59	−0.060 98
0.007	0.899	−0.125 66	−0.051 98	0.880	−0.124 15	−0.053 34	0.847	−0.119 95	−0.053 79	0.798	−0.113 94	−0.052 37
0.01	0.882	−0.108 32	−0.044 87	0.861	−0.106 94	−0.045 95	0.823	−0.103 10	−0.046 12	0.767	−0.097 65	−0.045 85
0.015	0.861	−0.088 72	−0.036 60	0.836	−0.087 62	−0.037 79	0.793	−0.084 17	−0.037 86	0.728	−0.079 50	−0.037 62
0.02	0.844	−0.074 96	−0.030 96	0.817	−0.074 02	−0.031 72	0.769	−0.070 97	−0.031 96	0.699	−0.066 80	−0.031 82
0.03	0.818	−0.055 74	−0.023 07	0.788	−0.055 04	−0.023 97	0.732	−0.052 67	−0.023 78	0.654	−0.049 39	−0.023 51
0.05	0.781	−0.031 87	−0.013 72				0.683	−0.029 98	−0.013 70	0.594	−0.028 08	−0.013 57
0.05	0.781	−0.031 87	−0.013 10*									
0.07	0.755	−0.016 32	−0.006 89	0.720	−0.016 14	−0.007 17	0.649	−0.015 31	−0.007 00	0.554	−0.014 38	−0.006 90
0.07				0.720	−0.016 14	−0.007 89*	0.649	−0.015 31	−0.006 69*	0.554	−0.014 38	−0.00 63*
0.15										0.468	0.016 12	0.007 85
0.15										0.468	0.016 12	0.007 3*
0.2	0.669	0.031 42	0.012 37	0.632	0.031 11	0.013 21	0.543	0.029 47	0.012 99	0.439	0.027 61	0.012 90
0.2	0.669	0.031 42	0.011 89*	0.632	0.031 11	0.012 70*	0.543	0.029 47	0.012 31*	0.439	0.027 61	0.012 6*
0.3										0.405	0.044 31	0.020 84
0.4										0.387	0.056 75	0.026 51
0.4										0.387	0.056 75	0.024 7*
0.5	0.602	0.073 08	0.030 19	0.566	0.072 52	0.030 40	0.472	0.069 35	0.030 37	0.378	0.067 01	0.031 00
0.5	0.602	0.073 08	0.028 74*	0.566	0.072 52	0.029 91*	0.472	0.069 35	0.029 29*	0.378	0.067 01	0.029 6*
0.7	0.583	0.088 72	0.036 59	0.549	0.088 25	0.036 65	0.458	0.085 10	0.036 90			
0.7	0.583	0.088 72	0.034 82*	0.549	0.088 25	0.036 13*	0.458	0.085 10	0.035 86*			
1	0.571	0.105 98	0.042 89	0.537	0.105 44	0.043 00	0.454	0.102 97	0.043 98			
1	0.571	0.105 98	0.041 37*	0.537	0.105 44	0.043 15*	0.454	0.102 97	0.043 94*			
1.5	0.569	0.126 63	0.050 87	0.534	0.125 98	0.051 08						
1.5	0.569	0.126 63	0.050 16*	0.534	0.125 98	0.051 34*						
2	0.579	0.142 31	0.056 20	0.543	0.141 63	0.058 00						
2	0.579	0.142 31	0.055 82*	0.543	0.141 63	0.057 07*						
2				0.543	0.141 63	0.057 52*						
3	0.619	0.166 58	0.065 97									
3	0.619	0.166 58	0.065 12*									
4	0.677	0.185 96	0.072 67									
4	0.677	0.185 96	0.071 60*									
0.1 (fixed)	0.726	(0)	(0)	0.690	(0)	(0)	0.612	(0)	(0)	0.513	(0)	(0)

[a] The mean molal activity coefficients γ of NaCl are taken from the literature (Basili et al.,1996). [b] The E_A values marked * have been obtained as $E_A = E_{MAX} - E_C$ (eq 3) from the measured emf's E_C of the transference cell Pt|Na$_X$Hg$_{1-X}$|NaCl(m_{fix})|NaCl(m_{var})|Na$_X$Hg$_{1-X}$|Pt.

to characterize new salt bridges, and thus the highest mass fraction w_M of methanol in the methanol + water mixtures explored here is 0.8, because at higher w_M's the solubility of the MeCl electrolyte becomes too low. However, both the silver/silver chloride and the Me-amalgam electrodes in the above cells would respond correctly also at w_M > 0.8. These

Table 3. emf's E_A of the Transference Cell Ag|AgCl|KCl (m_{var})|KCl (m_{fix})|AgCl|Ag, at 25 °C, as a Function of the Variable Molality m_{var}, in Methanol + Water Mixed Solvents of Methanol Mass Fractions w_M, with Corresponding E_{MAX} Values (Eq 4)

m_{var}/(mol·kg^{-1})	γ^a	E_{MAX}/V	$E_A{}^b$/V	γ^a	E_{MAX}/V	$E_A{}^b$/V	γ^a	E_{MAX}/V	$E_A{}^b$/V
0.002	0.942	−0.187 21	−0.094 64	0.929	−0.183 22	−0.094 26	0.911	−0.178 52	−0.091 71
0.005	0.912	−0.141 79	−0.071 76	0.892	−0.138 22	−0.071 24	0.865	−0.134 10	−0.069 24
0.007	0.898	−0.125 30	−0.063 45	0.875	−0.121 92	−0.062 67	0.844	−0.118 08	−0.060 93
0.01	0.882	−0.107 89	−0.054 71	0.854	−0.104 84	−0.052 90	0.819	−0.101 29	−0.052 44
0.02	0.843	−0.074 60	−0.038 00	0.806	−0.072 20	−0.037 67	0.760	−0.069 52	−0.035 80
0.03	0.816	−0.055 44	−0.028 44	0.773	−0.053 51	−0.027 95	0.721	−0.051 39	−0.026 89
0.05	0.778	−0.031 64	−0.016 27	0.726	−0.030 49	−0.016 03	0.667	−0.029 14	−0.015 39
0.05	0.778	−0.031 64	−0.016 44*	0.726	−0.030 49	−0.015 20*	0.667	−0.029 14	−0.015 23*
0.07	0.750	−0.016 23	−0.008 40	0.693	−0.015 59	−0.008 28	0.629	−0.014 86	−0.007 93
0.07	0.750	−0.016 23	−0.008 88*	0.693	−0.015 59	−0.007 36*	0.629	−0.014 86	−0.008 10*
0.2							0.509	0.028 20	0.014 74
0.2							0.509	0.028 20	0.014 09*
0.2032				0.584	0.030 38	0.015 80			
0.2032				0.584	0.030 38	0.014 66*			
0.3	0.620	0.048 77	0.024 90				0.468	0.044 72	0.023 17
0.3	0.620	0.048 77	0.024 30*				0.468	0.044 72	0.022 30*
0.5	0.575	0.071 15	0.036 19	0.504	0.069 08	0.035 27	0.425	0.066 02	0.033 59
0.5	0.575	0.071 15	0.035 31*	0.504	0.069 08	0.034 39*	0.425	0.066 02	0.033 02*
0.7	0.547	0.085 87	0.044 18	0.484	0.084 29	0.042 55			
0.7	0.547	0.085 87	0.041 98*	0.484	0.084 29	0.043 45*			
1	0.521	0.101 70	0.051 56	0.473	0.101 43	0.050 16			
1	0.521	0.101 70	0.050 66*						
1.6111	0.491	0.123 16	0.062 02						
1.6111	0.491	0.123 16	0.060 45*						
2	0.481	0.133 21	0.066 92						
0.1 (fixed)	0.720	(0)	(0)	0.657	(0)	(0)	0.588	(0)	(0)

[a] The mean molal activity coefficients γ of KCl are taken from the literature (Basili et al., 1997). [b] The E_A values marked * have been obtained as $E_A = E_{MAX} - E_C$ (eq 3) from the measured emf's E_C of the transference cell Pt|K_XHg_{1-X}|KCl (m_{Fix})|KCl (m_{Var})|K_XHg_{1-X}|Pt.

emf's must be combined with the emf E_{MAX} of the double cell (III) without transference:

$$\mathrm{Ag|AgCl|MeCl}\ (m_{var})|\mathrm{Me(Hg)}{-}\mathrm{Me(Hg)|MeCl}\ (m_{fix})|\mathrm{AgCl|Ag} \quad \text{(III)}$$

The revised theory and the related scheme of interpretation of these emf's have been described quite recently (Mussini et al., 1990a; Mussini et al., 1990b; Mussini et al., 1995; Mussini et al., 1998) and hinge on the following set of equations:

$$dE_A/dE_{MAX} = t_C(\mathrm{APP}) = t_C - \tau_S M_S m \quad (1)$$

$$dE_C/dE_{MAX} = t_A(\mathrm{APP}) = t_A + \tau_S M_S m \quad (2)$$

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

$$E_{MAX} = 2k \ln(m_{var}\gamma_{var}/m_{fix}\gamma_{fix}) \quad (4)$$

where t_C(APP) and t_A(APP) are the *apparent* transference numbers (viz. not cleared of the solvent-transfer contribution $\tau_S M_S m$) and t_C and t_A are the *true* transference numbers of the cation Me^+ and the anion Cl^- in the current definition, τ_S is the transfer number of the solvent S (in terms of moles of S transferred per Faraday inside the cell from the anode to the cathode), M_S is the molar mass (kg·mol^{-1}) of the solvent, γ_{var} and γ_{fix} denote the mean molal activity coefficients of MeCl at the respective molalities m_{var} and m_{fix} (mostly, $m_{var} > m_{fix}$), $k = RT/F$, R = gas constant, F = Faraday's constant, and T = absolute temperature. t_C (as well as t_A) complies with the Stokes−Robinson equation (Stokes, 1954; Robinson and Stokes, 1965a):

$$t_C = t_{Me^+} = [\lambda°_{Me^+} - {}^1/_2 B_2\sqrt{m}/(1 + a_0 B\sqrt{m})]/[\Lambda°_{MeCl} - B_2\sqrt{m}/(1 + a_0 B\sqrt{m})] = [t°_{Me^+} - 0.5]/\{1 - B_2\sqrt{m}/[(1 + a_0 B\sqrt{m})\Lambda°_{MeCl}]\} + 0.5 \quad (5)$$

where $t°_{Me^+} = \lambda°_{Me^+}/\Lambda°_{MeCl}$ is the limiting (infinite-dilution) transference number of the cation Me^+, B_2 and B are classical constants of the Debye−Hückel−Onsager theory, a_0 is the ion-size parameter, and $\lambda°_{Me^+}$ and $\Lambda°_{MeCl}$ are the limiting molar conductivities of Me^+ and MeCl in solvent S, respectively.

Experimental Section

The silver/silver chloride electrodes in cell I were prepared according to the bielectrolytic method (Ives and Janz, 1961b). The Me-amalgam electrodes in cell II, with Me = Li, Na, K, and Rb, are of the dilute flowing-amalgam type. The details for the electrolytic preparation of these amalgams (by cathodic deposition at a mercury pool from aqueous 0.5 mol·kg^{-1} LiOH, NaOH, KOH, and Rb_2CO_3, respectively) and the operation procedure of the M-amalgam electrodes, as well as for the design of the apparatus for the temperature control, are described in an earlier paper (Mussini and Pagella, 1971). All emf's were measured at 25 °C by means of a Type 619 Keithley digital electrometer. The accuracy of emf measurements was ±0.03 mV, and that of temperature control was ±0.05 °C. The MeCl solutions in methanol + water mixtures were prepared by mass from redistilled deionized water and the following chemicals: LiCl, Baker, analyzed, 99.7% purity; NaCl, Fluka, 99.5%; KCl, Carlo Erba, >99.5%; RbCl, Fluka, 99.5%; NaOH, Fluka, 99%; KOH, Carlo Erba, 99%; Rb_2CO_3, Fluka, 99%; and methanol (CH_3OH), Carlo Erba,

Table 4. emf's E_A of the Transference Cell Ag|AgCl|RbCl (m_{Var})|RbCl (m_{fix})|AgCl|Ag, at 25 °C, as a Function of the Variable Molality m_{var}, in Methanol + Water Mixed Solvents of Methanol Mass Fractions w_M, with Corresponding E_{MAX} Values (Eq 4)

	$w_M = 0.2$			$w_M = 0.4$		
m_{var}/(mol·kg^{-1})	γ^a	E_{MAX}/V	$E_A{}^b$/V	γ^a	E_{MAX}/V	$E_A{}^b$/V
0.002	0.942	−0.186 56	−0.096 42	0.930	−0.184 25	−0.095 82
0.005	0.912	−0.141 14	−0.073 09	0.894	−0.139 19	−0.075 56
0.007	0.897	−0.124 71	−0.064 51	0.877	−0.122 89	−0.064 37
0.01	0.880	−0.107 36	−0.055 79	0.857	−0.105 75	−0.056 24
0.02	0.840	−0.074 13	−0.038 44	0.812	−0.072 90	−0.038 13
0.05	0.772	−0.031 39	−0.016 79	0.737	−0.030 80	−0.016 23
0.05	0.772	−0.031 39	−0.015 43*	0.737	−0.030 80	−0.015 40*
0.07	0.743	−0.016 07	−0.007 92	0.705	−0.015 79	−0.008 00
0.07	0.743	−0.016 07	−0.008 28*	0.705	−0.015 79	−0.006 59*
0.2	0.644	0.030 53	0.015 82	0.601	0.029 96	0.015 42
0.2	0.644	0.030 53	0.015 65*	0.601	0.029 96	0.015 78*
0.5	0.555	0.069 97	0.036 60	0.510	0.068 60	0.035 60
0.5	0.555	0.069 97	0.034 10*	0.510	0.068 60	0.035 74*
0.7	0.525	0.084 41	0.044 07	0.478	0.082 56	0.042 80
0.7	0.525	0.084 41	0.044 07*	0.478	0.082 56	0.042 32*
1	0.495	0.099 71	0.051 83	0.447	0.097 45	0.050 42
1	0.495	0.099 71	0.050 96*	0.447	0.097 45	0.050 20*
2	0.450	0.130 43	0.067 30	0.394	0.126 58	0.065 90
2	0.450	0.130 43	0.066 42*	0.394	0.126 58	0.065 20*
3	0.434	0.149 41	0.076 53			
3	0.434	0.149 41	0.076 77*			
4	0.429	0.163 59	0.083 44			
4	0.429	0.163 59	0.084 85*			
5	0.431	0.175 30	0.088 83			
0.1 (fixed)	0.711	(0)	(0)	0.671	(0)	(0)

[a] The mean molal activity coefficients γ of RbCl are taken from the literature (Basili et al., 1997). [b] The E_A values marked * have been obtained as $E_A = E_{MAX} - E_C$ (eq 3) from the measured emf's E_C of the transference cell Pt|Rb$_X$Hg$_{1-X}$|RbCl (m_{fix})|RbCl (m_{var})|Rb$_X$Hg$_{1-X}$|Pt.

>99.9% (GLC), which was used as received, without further purification. The accuracy in the molality values was better than ±0.015%.

Results and Discussion

Tables 1−4 quote the emf E_A at 25 °C of cell I together with the parallel E_{MAX} results for cell III, as a function of the variable molality m_{var} of MeCl (Me$^+$ = Li$^+$, Na$^+$, K$^+$, and Rb$^+$) at fixed molality m_{fix} in the methanol + water mixtures with mass fractions w_M of methanol up to w_M = 0.8. The equilibration time needed for E_A to reach stabilization to ±0.01 mV was typically ≈40 min with the lowest MeCl molalities, ≈30 min with the intermediate molalities, and ≈20 min with the highest ones. 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 for the subsequent computational processing. E_{MAX} has not been measured but simply calculated through eq 4, since accurate activity coefficients γ for MeCl over the required molality ranges are available (Basili et al., 1996; Basili et al., 1997; Sala,-1999). Because those previously available for LiCl were not experimental but only estimated (Harned, 1962) and they did not cover the molality range studied here, for the methanol mass fraction w_M = 0.2, they have been freshly redetermined (Sala, 1999) from measurements of the emf E_{IV} of the lithium amalgam cell (IV):

$$\text{Pt}|\text{Li}_x\text{Hg}_{1-x}|\text{LiCl}\ (m)|\text{AgCl}|\text{Ag}|\text{Pt} \qquad \text{(IV)}$$

Table 5. emf's E_{IV} of Cell IV for the Determination of Mean Molal Activity Coefficients γ of LiCl at Various Molalities m in Methanol + Water Solvent Mixtures at Methanol Mass Fraction w_M = 0.2 at 25 °C, Together with the Relevant Parameters: Standard emf $E°_{IV}$, Debye−Hückel Constants A and B, Ion-Size Parameter a_0 and Interaction Parameters b and c, and Rational Activity Coefficients f_{Li} of Li Metal at Mole Fractions x_{Li} in the Amalgam Electrodes

$1000x_{Li}$	f_{Li}	M/(mol·kg^{-1})	E_{IV}/V	γ
3.294	1.075	0.00532	2.4112	0.914
3.294	1.075	0.1055	2.3795	0.749
6.284	1.147	0.1055	2.3956	0.749
3.294	1.075	0.2111	2.3464	0.709
6.284	1.147	0.3002	2.3463	0.694
3.294	1.075	0.5283	2.3012	0.685
6.284	1.147	0.6000	2.3119	0.677
3.294	1.075	1.0560	2.2620	0.723
6.754	1.159	1.9994	2.2406	0.870
6.754	1.159	2.9990	2.2074	1.112
6.754	1.159	5.0048	2.1514	1.947
6.754	1.159	8.9990	2.0566	6.919

$E°_{IV} = 2.3934$ V
$A = 0.5950$ kg$^{1/2}$·mol$^{-1/2}$
$B = 3.420$ kg$^{1/2}$·mol$^{-1/2}$·nm^{-1}
$a_0 = 0.3610$ nm
$b = 0.1366$ kg·mol^{-1}
$c = 0.00151$ kg^2·mol^{-2}
$M_S = 0.019744$ kg·mol^{-1}

The emf E_{IV} values, which are quoted in Table 5 as a function of m, together with the relevant parameters of the calculation, have been processed according to the familiar extrapolation function Φ:

$$\Phi = E_{IV} + 2k \log m - 2kA\sqrt{m}/(1 + a_0B\sqrt{m}) - 2k \log(1 + 2mM_S) - k \log(xf) = E°_{IV} - 2kbm - 2kcm^2 \qquad (6)$$

which results from combining the Nernstian expression for E_{IV} with the extended Debye−Hückel equation for the activity coefficients, the methodology being analogous to that previously used for the activity coefficients of NaCl,

Table 6. Limiting (Infinite Dilution) Transference Numbers $t°_{M^+}$ at 25 °C of Alkali Chlorides in Methanol + Water Solvent Mixtures of Methanol Mass Fractions w_M, Based on the emf's of the Transference Cells I and II, with Respective Standard Errors and Literature Data for Pure Water ($w_M = 0$) for Comparison

	$w_M = 0$	$w_M = 0.1$	$w_M = 0.2$	$w_M = 0.4$	$w_M = 0.6$	$w_M = 0.8$
$t°_{Li+}$	0.3363[a]	0.3291 ±0.0040	0.3316 ±0.0043	0.351[d]	0.367[d]	0.393[d]
$t°_{Na+}$	0.3962[a]		0.4171 ±0.0008	0.4273 ±0.0007	0.4462 ±0.0009	0.4680 ±0.0024
$t°_{K+}$	0.4895[b]		0.5069 ±0.0008	0.5117 ±0.0022	0.5155 ±0.0009	
$t°_{Rb+}$	0.5007[c]		0.5148 ±0.0013	0.5227 ±0.0019		

[a] Robinson and Stokes,1965b. [b] Longhi et al.,1990 [c] Buizza et al.,1996 [d] Interpolated from Longsworth and MacInnes,1939.

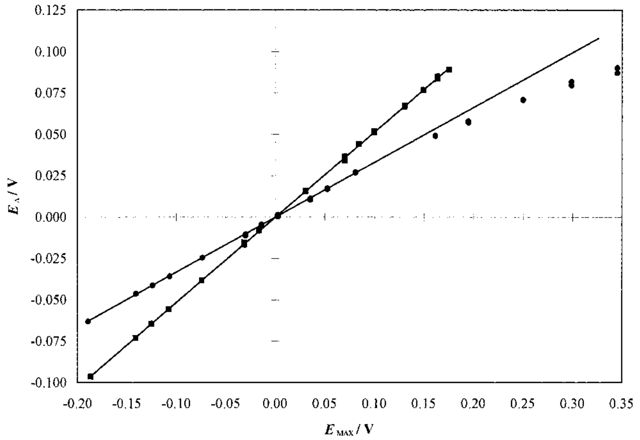

Figure 1. Relationship between E_A and E_{MAX} at 25 °C in methanol + water solvent mixtures at 0.2 mass fraction of methanol. (■) linear (RbCl); (●) asymptotic (LiCl).

KCl, and RbCl (Basili et al., 1996; Basili et al., 1997; Ceccattini et al., 1997). Using the parameters in Table 5, the γ's quoted in Table 1 have been interpolated at the required m's to obtain the corresponding E_{MAX}'s.

Figure 1 illustrates the relationship between E_A and E_{MAX} for LiCl and RbCl in methanol + water at $w_M = 0.2$ (NaCl behaves similarly to LiCl, and KCl behaves similarly to RbCl). While for RbCl a straight line covers the whole molality range, for LiCl the present results indicate a straight line at low and intermediate molalities which becomes a flat curve at higher molalities; that is, it really has an oblique asymptote, just as previously observed, for example, for NaCl in ethanol + water (Mussini et al., 1995). For these reasons, as also explained earlier (Mussini et al., 1995), we interpret the E_A relationship in terms of the following equation:

$$E_A = aE_{MAX} + b[1 - \exp(cE_{MAX})] \qquad (7)$$

From eqs 7 and 1 one gets

$$dE_A/dE_{MAX} = t_{Me^+}(APP) = t_{Me^+} - \tau_S M_S m = a - bc\exp(cE_{MAX}) \qquad (8)$$

and from eq 4 for E_{MAX} one can write

$$dE_A/dE_{MAX} = t_{Me^+}(APP) = t_{Me^+} - \tau_S M_S m_{var} = a - Q\,[(m_{var}\gamma_{var})_{MeCl}]^{2kc} \qquad (9)$$

where $Q = bc[(m_{fix}\gamma_{fix})_{MeCl}]^{-2kc}$ = constant at given temperature. Extrapolating eq 8 to infinite dilution ($m_{var} = 0$, $\gamma_{var} = 1$), one has $\tau_S M_S m_{var} = 0$ for the solvent-transfer term, and the limiting slope gives

$$(dE_A/dE_{MAX})_{m=0} = a = t°_{Me^+}(APP) \equiv t°_{Me^+} \qquad (10)$$

where $t°_{Me^+}$ is the limiting transference number of the cation Me^+. Typically $b < 0$ when $t°_{Me^+} > 0.5$, $b > 0$ when $t°_{Me^+} < 0.5$, and $b = 0$ when $t°_{Me^+} = 0.5$. When a rectilinear E_A versus E_{MAX} correlation over the whole molality range occurs (cases of RbCl and KCl), the exponential term in eq 9 is obviously dropped, and the slope of the experimental straight line directly gives the required limiting transference number, that is, $dE_A/dE_{MAX} = (dE_A/dE_{MAX})_{m=0} = a = t°_{Me^+}$, in keeping with eq 10. The found $t°_{Me^+}$ values are collected in Table 6. t_{Me^+} values at finite MeCl concentrations can, if desired, be calculated by eq 5 using the ancillary quantities and parameters quoted in Table 8. Since the present aim is to characterize new salt bridges, no attempt has been made at evaluating the solvent contribution $\tau_S M_S m_{var}$ by direct independent methods because it would have involved determination of distinct solvent-transference numbers for methanol (τ_M) and water (τ_W) in the mixtures, as well as distinct methanolation numbers (h_M) and hydration numbers (h_W) for MeCl.

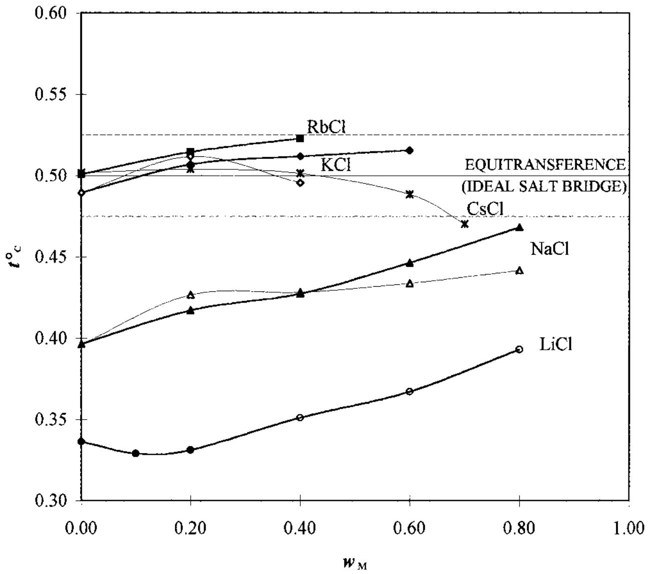

Figure 2. Emf-based limiting cationic transference numbers $t°_C$ at 25 °C of MeCl in (methanol + water) solvent mixtures, from the present work (*full points*, thick curves). The relevant uncertainties are quoted in Table 6. (○): moving-boundary values for LiCl (Longsworths and MacInnes, 1939); (△), (◇), and (∗): emf-based values for NaCl, KCl, and CsCl, respectively, in (ethanol + water) solvent mixtures (Mussini et al., 1995). The strip between dotted lines ($0.475 < t°_C < 0.525$) corresponds to acceptable limits of deviation (±5%) from the exact equitransference ($t°_C = t°_A = 0.5$) for MeCl salt bridges to be usable. For the present work, the relevant uncertainties are quoted in Table 6. Data in pure water ($w_M = 0$): LiCl and NaCl, Robinson and Stokes, 1965b; KCl, Longhi et al., 1990; RbCl, Buizza et al., 1996; CsCl, Mussini et al., 1990b.

Figure 2 compares the present $t°_{Me^+}$ results in methanol + water mixtures with some available data obtained by the moving boundary method (Longsworth and MacInnes, 1939; Shemilt et al., 1948), and with the analogous, recent ones obtained by the same emf methodology in ethanol + water (Mussini et al.,1995). It is evident that (1) in the w_M

Table 7. Limiting Molar and Ionic Conductivities $\Lambda°$ and $\lambda°/(\Omega^{-1}\cdot cm^2\cdot mol^{-1})$, for Alkali Chlorides at 25 °C in Various Methanol + Water Mixtures at Mass Fractions w_M of Methanol[a]

	$w_M = 0$	$w_M = 0.1$	$w_M = 0.2$	$w_M = 0.4$	$w_M = 0.6$	$w_M = 0.8$
$\Lambda°_{LiCl}$	115.09	*91.5*	*75.0*	*59.0*	*58.7*	*65.6*
$\lambda°_{Li^+}$	38.70	30.1	24.9	*20.7*	*21.5*	*25.8*
$\lambda°_{Cl^-}$	76.39	61.4	50.1	*38.3*	*37.2*	*39.8*
$\Lambda°_{NaCl}$	126.51		86.0	66.7	64.7	76.2
$\lambda°_{Na^+}$	50.12		35.9	28.5	28.9	35.7
$\lambda°_{Cl^-}$	76.39		50.1	38.2	35.8	40.5
$\Lambda°_{KCl}$	149.93		100.6	77.1	73.5	
$\lambda°_{K^+}$	73.54		51.0	39.5	37.9	
$\lambda°_{Cl^-}$	76.39		49.6	37.6	35.6	
mean $\lambda°_{Cl^-}$			49.9 ± 0.3	38.0 ± 0.4	36.2 ± 1.0	40.2 ± 0.4

[a] $\Lambda°$ values are from eq 12; $\lambda°$ values are from $\Lambda°$ and $T°$ in Table 5; data in pure water ($w_M = 0$) are quoted from the literature (Robinson and Stokes,1965b) for comparison; values interpolated from Longsworth and MacInnes (1939) are in italics.

Table 8. Relative Permittivities ϵ, Viscosities η, and Densities ρ at 25 °C of Methanol + Water Solvent Mixtures at Methanol Mass Fractions w_M, Required for Calculation of B and B_2 Constants, Together with Ion-size Parameters a_0 for LiCl, NaCl, and KCl, for Use in Eq 5

w_M	ϵ [a]	η[b]/(Pa·s)	ρ[c]/(kg°dm^{-3}) [c]	a_0(LiCl)/nm	a_0(NaCl)/nm [f]	a_0(KCl)/nm[f]
0.1	74.10	0.001 158	0.9799	0.411[d]		
0.2	69.95	0.001 400	0.9644	0.361[e]	0.296	0.299
0.4	59.60	0.001 593	0.9313		0.361	0.177
0.6	50.10	0.001 403	0.8912		0.262	0.163
0.8	40.14	0.001 006	0.8429		0.203	

[a] From Åkerlöf, 1932. [b] From Shedlovsky and Kay, 1956. [c] From Harned and Thomas, 1935; Oiwa, 1956; and Feakins and French, 1957. [d] Evaluated from Longsworth and Mac Innes,1939. [e] From Sala,1999. [f] From Basili et al., 1997.

range of common coverage, the agreement between the $t°_{Li^+}$ results from the two methods is good; (2) the general trend is for $t°_{Me^+}$ to increase with w_M, and it is much more pronounced for those Me$^+$s whose primary hydration sheaths are bigger (namely, Li$^+$ and Na$^+$) (an explanation for this behavior is given later on); (3) in particular, at $w_M = 0.8$ NaCl becomes almost as equitransferent as KCl in pure water ($w_M = 0$), so that in methanol + water it may act as a discrete salt bridge, a situation which would be quite inconceivable in pure water, where NaCl is too far from equitrasference;

(4) KCl becomes exactly equitransferent ($t°_{K^+} = t°_{Cl^-} = 0.5$), viz. an ideal salt bridge, at $w_M \approx 0.13$; (5) in the $t°_C$ versus w_M curve for LiCl the minimum at about w_M 0.15 is not unique: the same behavior pattern for LiCl is observed also, for example, in 1,4-dioxane + water solvent mixtures (Sala,1999); (6) the general MeCl behavior in methanol + water has remarkable similarities to that in ethanol + water (Mussini et al., 1995); and (7) both KCl and RbCl are proposable as salt bridges in methanol + water media, but they have the drawback of low solubilities (a situation met also in ethanol + water media (Mussini et al., 1995)), in contrast with the basic requirement of a "concentrated" equitransferent salt bridge (anyway, all the MeCl solubilities in methanol + water are seen to decrease with increasing w_M).

The trend described under (2) is brought about by preferential Me$^+$ solvation by the methanol added to water in increasing proportions, thus causing replacement of H_2O molecules of the Me$^+$ solvation sheath by methanol molecules. The negative end (an O atom) of the methanol dipole is attracted by Me$^+$; therefore, in the outer part of the solvation sheath, facing the bulk aqueous−organic mixed solvent, the net result is the replacement of an H atom of H_2O (susceptible to promoting hydrogen bonding) by a methanol molecule segment CH_3^-, which would instead reduce hydrogen bonding and thus favor an increase of Me$^+$ mobility with an ultimate increase of Me$^+$ transference number. The effect would be greater the higher the surface charge density of Me$^+$, that is greater with Li$^+$ than with Rb$^+$.

For the sake of comparison, Table 7 reports limiting molar ionic conductivities $\lambda°_{Me^+}$ and $\lambda°_{Cl^-}$ linked to the transference numbers $t°_{M^+}$ found in this work within the present w_M range, with the integration of some literature values. The relevant $\Lambda°_{MeCl}$ data are taken or interpolated from the literature (Amis, 1956; Butler et al., 1951; Harned and Owen, 1958; Janz and Tomkins, 1972a; Janz and Tomkins, 1972b; Jervis et al., 1951; Longsworth and MacInnes, 1939; Robinson and Stokes, 1965b; Schiff and Gordon, 1958), but $\Lambda°_{RbCl}$ values are hitherto lacking. For the purposes of interpolation, in the present context, the available $\Lambda°_{MeCl}$'s can be represented as a function of the methanol mass fraction w_M by the following polynomials:

$$\Lambda°_{LiCl}/(\Omega^{-1}\cdot cm^2\cdot mol^{-1}) = 115.05 - 274.26w_M + 405.66w^2_M - 175.07w^3_M$$

$$\Lambda°_{NaCl}/(\Omega^{-1}\cdot cm^2\cdot mol^{-1}) = 126.33 - 260.53w_M + 310.52w^2_M - 78.94w^3_M$$

$$\Lambda°_{KCl}/(\Omega^{-1}\cdot cm^2\cdot mol^{-1}) = 149.81 - 319.01w_M + 389.00w^2_M - 115.28w^3_M \quad (11)$$

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, shows three features: (i) the mobilities of the Li$^+$ and Na$^+$ ions are markedly lower than those of the other ions involved (K$^+$and Cl$^-$), which remain almost equal, at each solvent composition; (ii) the values of the limiting mobility (or, equivalently, of $\lambda°$) of Cl$^-$ for the salts considered turn out to be identical (with a mean deviation of about ±0.5 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$), which indicates complete dissociation for the above salts in all the solvent mixtures considered; and (iii) Stokes' radii $(r_{St})_{Li^+}$ and $(r_{St})_{Na^+}$ are always greater than the corresponding crystallographic radii $(r_{cr})_{Li^+}$ and $(r_{cr})_{Na^+}$, whereas for K$^+$ and Cl$^-$ the contrary is true. This implies that Li$^+$ and Na$^+$ have big primary solvation sheaths and that their mechanism of motion in methanol + water mixtures is one of viscous motion, unlike K^+ and Cl^-. The same behavior pattern occurs also in anhydrous methanol (not treated here because of lack of activity coefficients and too low solubilities for possible MeCl use as salt bridges), as can be inferred on the basis of some available moving-boundary results (Davies et al., 1951; Jervis et al., 1953).

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