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Transport Number of Ions in Water/DMF Solvents and Reference Electrode for Electrochemical Measurements in Nonaqueous Media

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The transport number of the ions, $t^{\pm}$, of $(C_2H_5)_4NClO_4$, $NaClO_4$, NaCl, KCl, and HCl in *N*,*N*-dimethylformamide(DMF)–water solvents were determined by the agar–salt bridge method. In order to compare this method, t^+(HCl)'s in DMF–water media were measured by both the Hittorf method and the concentration cell method. Good agreement among these methods leads to the conclusion that t^+(KCl) and t^-(KCl) are nearly equal in the whole range of DMF–water media. The results suggest that potentials obtained in nonaqueous polarography with the bridged SCE by correcting the bridge potential with a slow flowing type aqueous SCE are always referred to the ordinary aqueous SCE.

It is desirable that all potentials be referred to a common aqueous scale, such as the ordinary calomel electrode, regardless of the fact that the medium is aqueous or nonaqueous. A few attempts to do this in nonaqueous polarography have been made.[1–4] On prolonged immersion of an aqueous saturated potassium chloride salt bridge in a nonaqueous medium, a plug of solid KCl formed on the tip of the bridge and caused a significant increase in the resistance of the cell[2,3] and an increase in the liquid junction potential.[4] This resulted in a drift of the potential with time.

The use of the reference redox couple such as rubidium ion-rubidium amalgam,[5] ferricinum ion-ferrocene,[6] tris(phenanthroline)iron(II, III) complex,[7] $[Fe(bpy)_3]^+$–$[Fe(bpy)_3]^\circ$,[8] and the form R^--R^+ type[9] have an advantage for the purpose of comparing redox potentials of a given couple in different solvents. Those, however, are relative and contain some assumption concerning the solvation of couple ions or neutral particles.

Suitable reference electrodes in individual solvent systems are convenient,[10–13] but it is desirable, if possible, to use a common reference for emf measurements made in a variety of solvent systems.

In this connection, Fujinaga *et al.* have proposed a bridged SCE as an external reference electrode,[14] and polarographic behaviours of some compounds in the solvents of *N*,*N*-dimethylformamide (DMF)–water binary system have been studied with exact comparison of potentials referred to the bridged SCE.[15–18] One of the authors has investigated in detail the characteristics of the bridged SCE and emphasized its great utility,[19] showing that the potential drift during a period of polarographic scanning is less than 3 mV and that the potentials could be referred to the ordinary aqueous SCE with a precision of a few millivolts when the potentials were corrected for the bridged potential measured with a slow flowing-type aqueous SCE just after the scan was completed.

This conclusion is based on the coincidence of both the final bridge potential E_∞ and the calculated liquid junction potential $E_j(C_1, C_2)$ as tabulated in Table 1. The E_j were calculated by using the equation

$$E_j(C_1, C_2) = \frac{RT}{F}(t^- - t^+)\ln(C_2/C_1). \qquad (1)$$

The differences in transport number $(t^- - t^+)$ were obtained from the slope of the bridge potential E *vs.* log (C_2/C_1) plots at each DMF concentration. If the transport number thus obtained is right, all the voltammetric measurements with the bridged SCE are always referred to the common aqueous SCE, when a correction for the bridge potential is applied.

TABLE 1. BRIDGE POTENTIAL AND RECALCULATED LIQUID JUNCTION POTENTIAL[19]

$v_1=v_2$[a)]	C_1	C_2[b)]	E_0	E_∞[c)]	$(t^- - t^+)$[d)]	$E_j(C_1,C_2)$[e)]
0	0.1	0.24	11	4	0.160	3.6
40	0.1	0.5	38	8	0.174	7.2
70	0.1	0.5	75	14	0.268	11.1
100	0.1	0.5	122	38	0.773	32.0

a) The isometric volume % of DMF in the test soln(1) and in the tip of the bridge(2). b) Molarity of tetraethylammonium perchlorate (TEAP) in the test soln(1) and in the tip of the bridge(2). c) The bridge potential (mV) at the same day(0) and 30 d after the preparation of the bridge. d) Transport number of TEAP obtained from the slope of the E *vs.* log (C_2/C_1). e) Recalculated liquid junction potential at 25 °C by the help of Eq. 1.

In the present communication, the subject of the transport number was investigated in order to clarify the above point. The experimental methods available for measuring transport numbers fall into four categories: the Hittorf method, the concentration cell method, the moving boundary method, and the agar–salt bridge method.[20] The last of these is like that in the previous paper.[19] The purpose of this paper is, indeed, to compare the transport number obtained by the last method with those obtained by the first two methods.

Experimental

Preparation of the Test Solution in DMF–Water Media. Although it is a simple matter to prepare the solutions of a substance at various concentrations in different compositions of mixed solvent, it is difficult in practice to represent exactly and simultaneously both the solute and solvent composition. The present paper has solved this problem by introducing an isometric volume concentration, by which can be expressed a molarity, C, for the solute and a volume percent of either solvent composition. The conversion of the isometric volume percent to a weight percent or a mole fraction is easy.

Suppose a mixed solvent is prepared by adding V_A and V_B cm³ of pure solvents A and B whose densities d_A and d_B, respectively. Then the total volume V_o whose density d is

$$V_A d_A + V_B d_B = V_0 d. \tag{2}$$

When weight percent w_i and mole fraction X_i of solvent i are introduced into Eq. 2, we have

$$\frac{V_A}{V_o} = \frac{d}{d_A}\frac{w_A}{100} = \frac{d}{d_A}\frac{X_A M_A}{X_A M_A + X_B M_B}. \tag{3}$$

Equation 3 contains two unknown variables w_i and d, or X_i and d. Since the relation between w_i and d is measured experimentally, the isometric volume percent $v_i = 100\ V_i/V_o$ is easily converted to a weight percent w_i or mole fraction X_i. The conversion table for DMF–water binary system is shown in Table 2.

TABLE 2. RELATION BETWEEN THE ISOMERIC VOLUME PERCENT AND WEIGHT PERCENT OR MOLE FRACTION IN DMF–WATER MEDIA AT 25 °C

DMF wt% w_B	d[a]	Mole fraction of water, X_A	v_A	v_B[b]
0	0.9971	1.0000	100.00	0.00
5	0.9972	0.9869	95.01	5.28
10	0.9971	0.9733	90.00	10.56
15	0.9973	0.9583	85.02	15.85
20	0.9972	0.9419	80.01	21.13
25	0.9974	0.9260	75.02	26.42
30	0.9976	0.9044	70.04	31.71
35	0.9979	0.8828	65.05	37.00
40	0.9982	0.8588	60.07	42.30
45	0.9989	0.8322	55.10	47.62
50	1.0023	0.8022	50.26	53.09
55	1.0026	0.7685	45.25	58.42
60	1.0017	0.7301	40.18	63.67
65	0.9964	0.6860	34.98	68.62
70	0.9911	0.6349	29.82	73.50
75	0.9849	0.5749	24.70	78.26
80	0.9784	0.5035	19.62	82.92
85	0.9714	0.4172	14.61	87.48
90	0.9637	0.3107	9.67	91.89
95	0.9534	0.1759	4.78	95.96
98	0.9476[c]	0.0765	1.90	98.38
99	0.9457[c]	0.0394	0.95	99.19
99.9	0.9440[c]	0.0040	0.10	99.91
100	0.9439[d]	0.0003	0.01[d]	99.99

a) Density (g/cm^3) of the mixed solvent from Ref. 21. b) Isometric volume % of water (A) and DMF (B). c) Values obtained by interpolating between $w_B = 95$ and 100%. d) Ref. 26.

Electrolyte solutions were prepared, for example, by pipetting adequate amounts of aqueous stock solution of electrolyte and V_B cm^3 of pure DMF, and then diluting with water in a V_o cm^3 volumetric flask. After reaching room temperature or thermostat temperature, the decrement is adjusted by adding water. Since the conductance of hydrochloric acid solutions in DMF–water media varies with time after its preparation, the potential measurement for the HCl solutions was carried out one day after preparation. In this paper, DMF volume percent means thus $v_B = 100\ V_B/V_o$, unless otherwise stated. This method is convenient to prepare a series of sample solutions with changing solute concentration and/or in varying solvent composition, contineously.

All electrolytes used were of extra-pure reagent grade. The solvents were purified as described previously.[14] Even 100% DMF contains water about 0.03% (*cf.* Table 2) in this experiment.

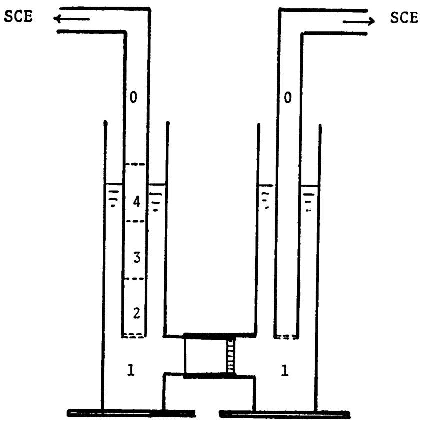

Fig. 1. Bridge potential measurement.
Phase 0, aq satd. KCl soln; 1, test soln (C_1, v_1); 2, DMF agar-salt bridge (C_2, v_2); 3, aq 0.5 M NaClO$_4$ agar bridge; 4, aq 1 M NaCl agar bridge.

Measurement of Transport Number. ***The Agar–Salt Bridge Method***: Figure 1 shows the experimental set-up for measuring the bridge potential E. The agar–salt bridge, dipping into the left compartment of the H-type cell in the figure, was prepared according to the previous paper,[19] and the compositions in phase 2 are shown in Table 3. When not in use, the end of the phase 2 side of the bridge was stored in the renewed preserving solution, having $C_2 = 0.1$ mol/dm^3 of the electrolyte and v_2 volume percent of DMF. A reference bridge, in the right-hand comaprtment, was an aqueous solution saturated with potassium chloride, which was allowed to flow very slowly into the test solution of phase 1, so as not to plug the tip of the bridge.

TABLE 3. COMPOSITION OF THE PHASE 2

Electrolyte	$\frac{C}{\text{mol dm}^{-3}}$	DMF vol%, v
TEAP[a]	0.1	0, 40, 70, 100
NaClO$_4$	0.1	0, 40, 70, 100
NaCl	0.1	0, 40, 70, 100
KCl	0.1	0, 40, 70, 100
HCl	0.1	0, 40, 70, 85

a) Tetraethylammonium perchlorate.

In Fig. 1, the cell is filled with a test solution (phase 1) which consists of C_1 mol/dm^3 of an electrolyte and v_1 % of DMF. The potential difference E between two SCE's was measured within one minute after both bridges have been dipped at the same time (or the agar bridge later than the reference) into the test solution. The E's were measured every time in renewed test solution under the condition of various electrolyte concentrations C_1 but $C_2 = 0.1$ and at various DMF contents, but v_1 was always equal to v_2. In each DMF solvent, the E's thus obtained were plotted against log (C_2/C_1); the slope gives the difference of transport number of anion and cation by the equation

$$t^- - t^+ = \frac{F}{RT}\frac{\mathrm{d}E}{\mathrm{d}\ln(C_2/C_1)}. \tag{4}$$

The Hittorf Method: For simplicity in the determination, only hydrochloric acid was chosen as an electrolye in this method.

Two 1×1 cm^2 platinum plates were used as electrodes. The copper coulometer consisted of 150 g of copper sulfate, 50 cm^3 of 3 M sulfuric acid, 50 cm^3 of ethanol and 1 dm^3 of pure water. Electrolyses were performed at room temperature, and the electrolysis time was fixed between 90—150 min.

Volumetric determination of HCl concentration in both compartments, cathode and middle, was carried out by titration with aqueous sodium hydroxide solutions with phenolphthalein as an indicator, using a microburette. Since the color change at end-point was not clear in the solution containing more than 70% DMF, the solution were diluted with water appropriately. The decrement of HCl in the cathode compartment, Δn_c, is calculated by

$$\Delta n_c = (V_m - V_c)\frac{1}{b}N\frac{V}{1000}, \qquad (5)$$

where V_m and V_c are the titer of N normality NaOH solution for b cm^3 of the respective middle and cathode compartments, V is the total amount in the cathode compartment. Hence the transport number of H$^+$ in HCl solution is

$$t^+(\mathrm{HCl}) = 1 - \Delta n_c\cdot\frac{F}{Q}, \qquad (6)$$

where Q is the amount of electricity passed through the coulometer and F the Faraday constant.

The Concentration Cell Method: The potential E of Cell-1 without liquid junction

$\mathrm{Ag|AgCl|HCl}(C_1)\mathrm{|H_2(Pt)|HCl}(C_2)\mathrm{|AgCl|Ag}$ Cell-1

and the potential E_t of Cell-2 with liquid junction

$\mathrm{Ag|AgCl|HCl}(C_1) \vdots \mathrm{HCl}(C_2)\mathrm{|AgCl|Ag}$ Cell-2

are expressed by the equations

$$E = \frac{2RT}{F}\ln\frac{a_\pm(C_1)}{a_\pm(C_2)} \qquad (7)$$

$$E_t = t^+\frac{2RT}{F}\ln\frac{a_\pm(C_1)}{a_\pm(C_2)}. \qquad (8)$$

In each solution having a definite DMF content, the logarithmic terms in Eq. 7 and 8 are equal, hence the combination of the two equations gives a transport number

$$t^+(\mathrm{HCl}) = E_t/E. \qquad (9)$$

Since the hydrogen electrodes and the silver-silver chloride electrodes have asymmetry potentials ΔE_h and ΔE_t, respectively, the equation 9 must be replaced in practice by

$$t^+(\mathrm{HCl}) = \frac{E_{t,\exp}-\Delta E_t}{E_{\exp}-(E_h-\Delta E_t)}. \qquad (10)$$

Potential measurements were made with a Shimadzu Precision Potentiometer K-2 Type. The hydrogen electrodes, 1×1 cm^2 platinum plates, and Ag-AgCl electrodes, the electrolytic type and the thermal-electrolytic type, were prepared and stored according to the accepted methods.[22–24] The latter were kept in water saturated with AgCl for 3 d (for use in water) and 7 d (for use in DMF–water media) after preparation, in order to stabilize the asymmetry potential $\varDelta E_t$.

For the $E_{\exp}$ and $E_{t,\exp}$ measurements, the cell consists of four compartments (A, B, C, and D) connecting to a four-way stopcock. Two test solutions C_1 and C_2, whose DMF contents were the same, were placed in the compartments A, C and B, D, respectively. To A and B an appropriate amount of AgCl powder was added and stirred to saturate, and then the Ag-AgCl electrodes were inserted. The hydrogen electrodes were put into C and D compartments. The four compartments were bubbled with hydrogen gas (purified through pyrogallol solution) for 30—60 min. After the bubbling, the compartments A-C and B-D were connected by turning the four-way stopcock and the potential difference $E_{\exp}$ between A and B was measured (Cell-1). When two hydrogen electrodes were exchanged for a salt bridge or when the two compartments A and B were connected by the stopcock, the potential corresponds to $E_{t,\exp}$ (Cell-2).

The asymmetry potentials ΔE_h and ΔE_t were measured before each $E_{\exp}$ measurement, using, an H-type cell in which the concentrations of electrolyte in both compartments were fixed at C_2 and the other concentrations were the same as in the measurement of $E_{\exp}$. The ΔE_t potentials have large values just after the Ag–AgCl electrodes have been transferred to DMF–water media from the aqueous preserving solution, but they decrease with time and stabilize after about half an hour in water and 1 h in DMF, respectively. The addition of solid AgCl is necessary because the silver chloride of the electrode is dissolved in DMF.[25]

Results

The Agar–Salt Bridge Method. The bridge potentials E were measured at room temperature by changing the electrolyte concentration C_1 of the test solution under the condition of $v_1 = v_2$. The results of plotting the E *va.* log (C_2/C_1) for several electrolytes at DMF contents of 0, 40, 70% and DMF-rich solutions are

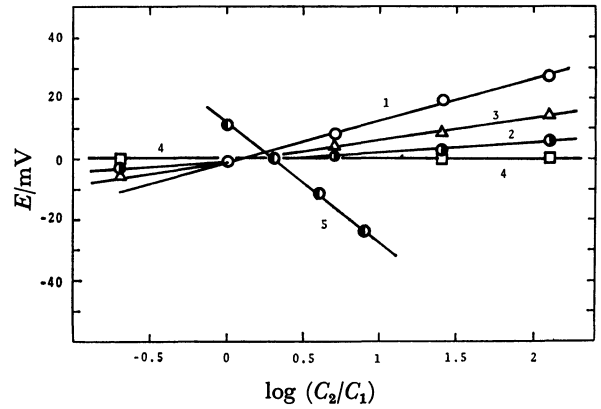

Fig. 2. Plots of E *vs.* log (C_2/C_1) at $C_2 = 0.1$ in water. Electrolyte: curve 1, TEAP; 2, NaClO$_4$; 3, NaCl; 4, KCl; 5, HCl.

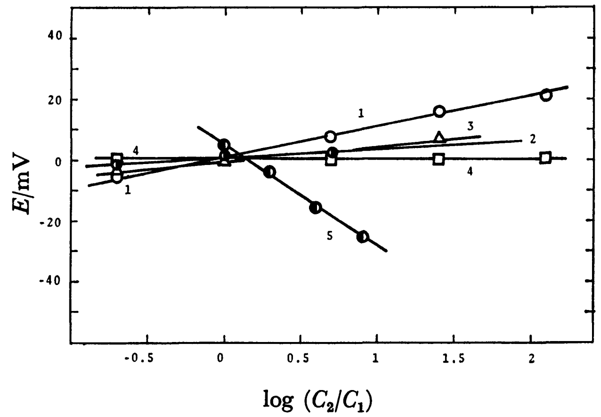

Fig. 3. Plots of E *vs.* log (C_2/C_1) at $C_2 = 0.1$ in 40% DMF. Electrolyte: curve 1, TEAP; 2, NaClO$_4$; 3, NaCl; 4, KCl; 5, HCl.

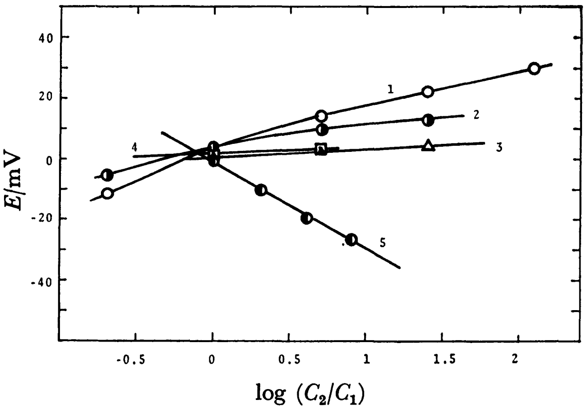

Fig. 4. Plots of E vs. log (C_2/C_1) at $C_2=0.1$ in 70% DMF. Electrolyte: curve 1, TEAP; 2, $NaClO_4$; 3, NaCl; 4, KCl; 5, HCl.

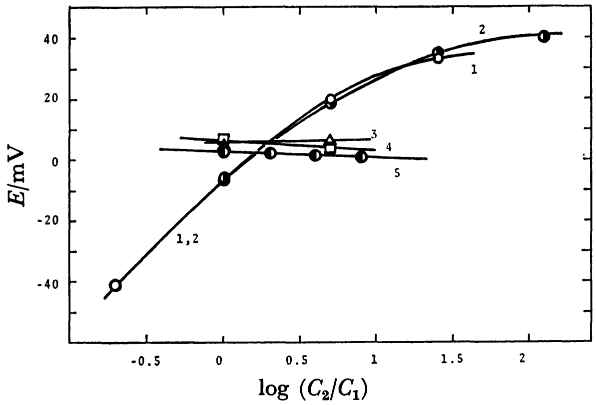

Fig. 5. Plots of E vs. log (C_2/C_1) at $C_2=0.1$ in DMF-water.
Electrolyte: curve 1, TEAP in DMF; 2, $NaClO_4$ in DMF; 3, NaCl in DMF; 4, KCl in DMF; 5, HCl in 85% DMF.

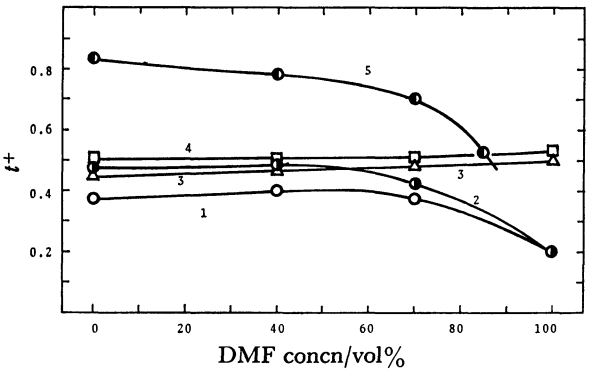

Fig. 6. Transport number of cations t^+ by the Agar-salt bridge method in DMF-water media at room temperature.
Electrolyte; curve 1, TEAP; 2, $NaClO_4$; 3, NaCl; 4, KCl; 5, HCl.

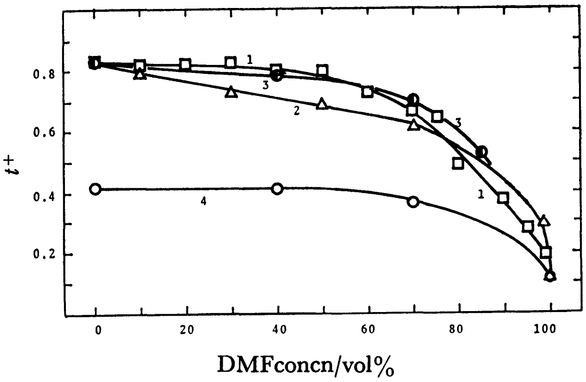

Fig. 7. Comparison of different methods of transport number in DMF-water media.
Curve 1, Hittofrt method t^+(HCl) at $C=0.1$, 2 Concn cell method t^+(HCl) at $C=0.01$—0.0005; 3, Agar-salt bridge method t^+(HCl) at $C=0.1$—0.02 from Fig. 6; 4, Agar-salt bridge method t^+(TEAP) at $C=0.5$—0.1.[19]

shown in Figs. 2, 3, 4, and 5, respectively. From these figures, one sees that good linear relations are found, except for tetraethylammonium perchlorate (TEAP) in solutions DMF content above 70% (curve 1 in Figs. 4 and 5) and for $NaClO_4$ in DMF (curve 2 in Fig. 5). By taking the slope between 0 and 0.7 in the abscissa and introducing this slope into Eq. 4, the transport number was calculated. In this way, the transport numbers of cation t^+ in each electrolyte were plotted against DMF content as shown in Fig. 6.

The Hittorf Method. Measurements were carried out at room temperature at a concentration of hydrochloric acid about 0.1 mol/dm^3 and in the range of DMF content $v=0$—99%. The amounts of electricity (Q) passed through the cell for a definite time were decreased with increase of DMF content from 50 coulombs in water to about 4 coulombs in 99% DMF media. The values of t^+(HCl) varied from 0.825 in water to 0.188 in 99% DMF media. A plot of the t^+(HCl) against DMF content is shown as curve 1 in Fig. 7.

The Concentration Cell Method. In order to compare with the Hittorf method, hydrochloric acid in DMF-water media was studied by this concentration cell method. All the cell electromotive forces E_{exp} and $E_{\mathrm{t,exp}}$ were measured at the condition of $C_1=2C_2$, and the asymmetry potentials ΔE_{h} and ΔE_{t} were measured at the lower concentration of C_2. The data tabulated in Table 4 were obtained with a Ag-AgCl electrode made by the electrolytic method. The plot of these average values t^+(HCl) against the DMF content is shown as curve 2 of Fig. 7.

The t^+ in 99.9 wt% of DMF, about 0.11, is quite uncertain, due possibly to a failure of the hydrogen electrodes. From the limiting ionic conductances $\lambda_0(\mathrm{Cl}^-)=55.1$[26] and $\Lambda_0(\mathrm{HCl})=(79.3+70+75.5)/3\doteqdot 74.9$,[27] the calculated transport number of the proton in hydrochloric acid in most carefully purified DMF is 0.26, a value obtained by dividing the difference $\Lambda(\mathrm{HCl})-\lambda_0(\mathrm{Cl}^-)$ by the $\Lambda_0(\mathrm{HCl})$.

Discussion

Curves 1, 2, and 3 in Fig. 7 are transport numbers of the proton of HCl in DMF-water media, obtained by the three methods. Because of the dissimilarity in

Table 4. Transport number of the proton of HCl by the concentration cell method at $C_1=2C_2$ inDMF–water media at 24 ± 0.5 °C

DMF vol% v_B	C_1 mol dm^{-3}	Emf/mV ΔE_h	ΔE_t	E_{exp}	$E_{t,ext}$	t^+(HCl)
0	0.01	0.03	0.11	25.78	21.28	0.8257
	0.005	0.07	0.12	22.37	18.41	0.8246
	0 001	0.03	0.13	21.91	18.06	0.8244
	0.0005	0.02	0.07	21.75	17.92	0.8241
10	0.01	0.03	0.41	21.14	17.01	0.8019
	0.005	0.06	0.38	22.63	17.43	0.7684
	0.001	0.08	0.40	22.18	17.87	0.8051
	0.0005	0.07	0.41	20.97	16.94	0.8067
30	0.01	0.05	0.98	20.66	15.41	0.7351
	0.005	0.08	0.90	19.43	14.41	0.7322
	0.001	0.09	1.00	20.27	14.98	0.7289
	0.0005	0.12	1.09	20.39	15.11	0.7310
50	0.01	0.03	0.50	17.04	11.78	0.6832
	0.005	0.09	0.49	16.72	11.40	0.6760
	0.001	0.08	0.48	16.26	11.31	0.6898
	0.0005	0.10	0.68	17.71	12.19	0.6799
70	0.01	0.09	0.69	16.22	8.56	0.5097
	0.005	0.10	0.68	15.64	8.26	0.5101
	0.001	0.12	0.65	16.43	8.46	0.4987
	0.0005	0.11	0.68	16.91	9.22	0.5298
98	0.0113	0.03	0.83	8.48	3.25	0.318
	0.0055	0.12	0.78	12.54	3.98	0.275
	0.0011	0.12	0.96	11.55	4.05	0.295
	0.0006	0.07	0.87	8.78	3.05	0.275
99.9[a)]	0.0113	0.05	0.98	6.40	1.38	0.075
	0.0055	0.07	1.03	4.11	1.48	0.150
	0.0011	0.03	0.95	5.14	1.47	0.125
	0.0006	0.04	0.83	5.72	1.23	0.083

a) Weight percent.

the concentration and in the temperature, a precise comparison among them is difficult. Nevertheless, one may conclude that the method of the agar–salt bridge (curve 3 in Fig. 7) is consistent with the other two methods (curves 1 and 2) of measuring the transport number. Consequently, the transport numbers shown in Fig. 6 for different electrolytes and the t^+(TEAP) in curve 4 of Fig. 7 (taken from the reference 19) are also correct.

It may be noted that curve 4 of Fig. 6 shows that the transport numbers t^+(KCl) and t^-(KCl) are nearly equal in the whole range of DMF–water binary solutions. Thus the liquid junction potential E_j is expected to be zero in terms of Eq. 1 for KCl solutions.

From the above discussion, it can be concluded that potentials obtained in nonaqueous polarography with a slow flowing-type aqueous SCE can be referred to the ordinary aqueous SCE exactly within a few millivolts.

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