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ELECTROCHEMICAL CHARACTERISTICS OF TRIFLUOROMETHANESULPHONIC ACID AND ITS SALTS IN NON-AQUEOUS SOLVENTS

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Analytical Chemistry Division

Commission on Electroanalytical Chemistry*

ELECTROCHEMICAL CHARACTERISTICS OF TRIFLUOROMETHANESULPHONIC ACID AND ITS SALTS IN NON-AQUEOUS SOLVENTS

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Abstract- Electrochemical characteristics of trifluoromethanesulphonic acid and its salts in non-aqueous solvents are reviewed. Topics discussed include dissociation equilibria and the electrochemical use as supporting electrolyte. These characteristics are also compared with those of perchloric acid and other sulphonic acids such as *p*-toluenesulphonic, methanesulphonic, and fluorosulphuric acids.

INTRODUCTION

Trifluoromethanesulphonic acid was synthesized for the first time by Haszeldine and Kidd (Ref. 1) in 1954 by the oxidation of bis (trifluoromethylthio) mercury with aqueous hydrogen peroxide. It is a colourless, very hygroscopic, mobile liquid which boils at a considerably lower temperature (162°C at 760 mm Hg) than does methanesulphonic acid (165°C at 8.5 mm Hg). The following values have been cited (Ref. 2) for the density, refractive index, viscosity, electrolytic conductivity, and dielectric constant at 25°C for the pure acid: $d = 1.6980\ \mathrm{g\ cm^{-3}}$, $n_D^{25} = 1.3250$, $\eta = 2.87$ cP ($1\mathrm{cP} \equiv 10^{-3}\ \mathrm{Kg\ m^{-1}\ s^{-1}}$), $\kappa = 2 \times 10^{-4}\ \mathrm{S\ cm^{-1}}$ [$3.5 \times 10^{-5}\ \mathrm{S\ cm^{-1}}$ (Ref. 3)], and D = 38 (Ref. 3), respectively.

Trifluoromethanesulphonic acid has often been claimed to be the strongest of Brönsted acids known (Ref. 1 and 4). However, this includes some uncertainty because there is no unique order of acidities of strong Brönsted acids independent of solvent media. For example, the following order of acid strengths has been reported on the basis of conductometric studies: $CF_3SO_3H > HClO_4 > HBr > HI > FSO_3H > H_2SO_4 > HCl$ in acetic acid (Ref. 5), and $FSO_3H > ClSO_3H \sim CF_3SO_3H \gg HClO_4$ in sulphuric acid (Ref. 6). In practice, trifluoromethanesulphonic acid and its conjugate base, trifluoromethanesulphonate anion, have some advantages in comparison with other strong acids. The acid and its anion show remarkable resistance to thermal decomposition and hydrolysis (Ref. 1, 7 and 8). The stability of the trifluoromethanesulphonate anion is also shown by the fact that it is a facile leaving group in solvolytic displacement reactions (Ref. 9–11): methyl trifluoromethanesulphonate undergoes acetolysis 10^4 times as rapidly as methyl *p*-toluenesulphonate (Ref. 9). Moreover, trifluoromethanesulphonic acid is a particularly well-suited solvent to the study of strong oxidation reactions (Ref. 3), and its anion is a very weakly coordinating ligand in aqueous solutions (Ref. 12). Trifluoromethanesulphonate anion can be an excellent alternative to ClO_4^-, BF_4^-, PF_6^- and so on, because of its stability and nonoxidizing nature (Ref. 13–16). Consequently extensive studies on trifluoromethanesulphonic acid and its derivatives have been performed in the last two decades, especially in organic chemistry, and they have recently been reviewed comprehensively by Howells and McCown (Ref. 2).

This communication reviews electrochemical characteristics of trifluoromethanesulphonic acid and its salts in non-aqueous solvents.

DISSOCIATION EQUILIBRIA

Dissociation of acid in dipolar aprotic solvents

Trifluoromethanesulphonic acid itself is stable to at least 350°C, and its aqueous solution is stable to at least 275°C (Ref. 7). In addition to being mixed with water in any proportions, the acid is soluble in many dipolar aprotic solvents such as dimethyl sulphoxide (DMSO), N, N-dimethylacetoamide (DMA), N, N-dimethylformamide (DMF), propylene carbonate (PC), acetonitrile (AN), sulpholane and so on. It is also soluble in alcohols, ethers, esters, and ketones, but

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these are not inert solvents, because further reaction often occurs, particularly on heating. This section describes the dissociation behaviour of trifluoromethanesulphonic acid in dipolar aprotic solvents and compares it with that of other strong acids.

The dissociation constants of trifluoromethanesulphonic acid have been evaluated in many aprotic solvents and are given in Table 1 together with values for other sulphonic acids. These values were determined mainly by conductometry. As shown in Table 1, all these acids (perchloric, trifluoromethanesulphonic, fluorosulphuric, *p*-toluenesulphonic, and methanesulphonic acids) are strong acids in DMSO, DMA, and DMF, which are rather basic in nature. In less basic solvents such as BuN, PC, sulphodane, and AN, trifluoromethanesulphonic and perchloric acids still behave as strong acids, while other sulphonic acids are weak acids. Especially in PC and AN, *p*-toluenesulphonate and methanesulphonate anions homoconjugate with the corresponding undissociated acids (Ref. 17, 23, 24 and 28). The conductivities of solutions of fluorosulphuric acid decrease slowly with time in BuN (Ref. 17), PC (Ref. 17 and 21), sulpholane (Ref. 22), and AN (Ref. 17). This may be due to reactions of fluorosulphuric acid with the trace water in the solvent (hydrolysis) and with the solvent itself to form some added product as reported in acetic acid (Ref. 29). Dimerization or polymerization of fluorosulphuric acid may also be considered in these solvents (Ref. 22). When perchloric acid is used as a dihydrate or an anhydrous one treated with acetic acid and acetic anhydride, the dissociation constant is only approximate because the water or acetic acid involved may have much influence on the dissociation equilibrium, particularly in less basic solvents (Ref. 31 and 81–84). In this regard, the differences of the dissociation constants of the same acid in Table 1 may be attributed to the differences of the water contents in the same solvent. Dimerization of trifluoromethanesulphonic acid in AN has been reported by Kolthoff and Chantooni (Ref. 32), while this is not observed in rather dilute solutions (Ref. 17).

TABLE 1. Dissociation constants (K_{HA}/mol dm^{-3}) of some sulphonic acids in dipolar aprotic solvents at 25°C

Acid	pK_{HA} in solvents						
	DMSO	DMA	DMF	BuN[h]	PC	sulpholane	AN
CF_3SO_3H	*[a,b] 0.59[c]	0.68[a]	*[a]	3.58[a]	1.31[a] 2.2[n]	3.4[b]	2.60[a]
FSO_3H	1.01[a]	1.08[a]	1.59[a] 2.12[d]	5.6[a]	4.66[a] 2.0[e]	3.3[f]	3.38[a]
$CH_3C_6H_4SO_3H$	0.90[a]	1.94[a]	2.23[a] 2.55[d] 2.59[j]	6.89[a]	6.38[a]		8.01[a]
CH_3SO_3H	1.56[a] 1.76[b] 1.63[c]	2.63[a]	2.98[a]	6.94[a]	7.21[a] 8.27[i]		8.36[a] 10.0[g]
$HClO_4$	1.03[a] 0.52[c] *[m]	0.78[a]	*[a]	2.67[a]	*[a] 1.3[o]	2.7[f] 3.0[k]	1.57[a] *[l]

* Completely dissociated. [a] Ref. 17. [b] Ref. 18. [c] Ref. 19. [d] Ref. 20. [e] Ref. 21. [f] Ref. 22. [g] Ref. 23. [h] *n*-butyronitrile [i] Ref. 24. [j] Ref. 25. [k] Ref. 26. [l] Ref. 27. [m] Ref. 30. [n] Ref. 81. [o] Ref. 82.

The following order of acid strengths is obtained and consistent in all the aprotic solvents in Table 1: $HClO_4 > CF_3SO_3H > FSO_3H > CH_3C_6H_4SO_3H > CH_3SO_3H$. Due to the low dielectric constants of these non-aqueous solvents, interionic attractions will be much more important than in water (Ref. 33). Consequently, the dissociation of an acid actually occurs in two steps,

$$\mathrm{HA} \underset{\text{Ionization}}{\overset{K_I}{\rightleftharpoons}} \mathrm{H^+A^-} \underset{\text{Dissociation}}{\overset{K_D}{\rightleftharpoons}} \mathrm{H^+ + A^-} \qquad (1)$$

the first of which produces the corresponding ion-pair which then dissociates into the separate ions. From conductometric or potentiometric measurements, only the overall dissociation constant, K_{HA}, can be determined,

$$K_{HA} = [H^+][A^-]f_{\pm}^2/([HA] + [H^+A^-]) = K_I K_D/(1 + K_I) \qquad (2)$$

where $K_I = [H^+A^-]/[HA]$ and $K_D = [H^+][A^-]f_{\pm}^2/[H^+A^-]$. Thus the overall dissociation constant is a function of K_I and K_D. The order of acid strengths obtained in dipolar aprotic solvents may reflect the charge densities of the anions: the ionization of an acid with anion of smaller charge density occurs to a greater extent, and the dissociation of the resulting ion-pair is also facilitated because only a large anion with a small charge density can be easily stabilized in aprotic solvents (Ref. 34). As the trifluoromethanesulphonate anion has the strong electronwithdrawing group (Ref. 35) CF_3, the magnitude of charge density of the anion is considered to be very close to that of perchlorate and much smaller than that of *p*-toluenesulphonate or methanesulphonate. Thus, trifluoromethanesulphonic acid, like perchloric acid, behaves as a strong acid in most dipolar aprotic solvents.

In the solvent of low dielectric constant methylene chloride, the equilibrium constant of the reaction $2HA \rightleftharpoons H_2A^+ + A^-$ was evaluated as 7.2×10^{-3} for CF_3SO_3H and 9.8×10^{-2} for FSO_3H, on the basis of polarographic measurements (Ref. 88).

Dissociation of trifluoromethanesulphonate salts in dipolar aprotic solvents

Trifluoromethanesulphonate salts of alkali (Ref. 1 and 36), alkaline earth (Ref. 1 and 37), transition metals (Ref. 1 and 37–39), and rare earth metals (Ref. 40) are easily prepared by the reaction of trifluoromethanesulphonic acid with metal hydroxide, carbonate, or oxide. These salts can be recrystallized from various solvents such as water, acetone, ethyl alcohol, and some organic solvent mixtures, and dehydrated at 100 – 150°C under vacuum. Tetraalkylammonium trifluoromethanesulphonates are also prepared by the method similar to corresponding perchlorates (Ref. 16, 36 and 37). These trifluoromethanesulphonates are more advantageous in preparation and purification than corresponding perchlorates and fluorosulphates (Ref. 41–43) because of their resistance to thermal decomposition and hydrolysis, and their non-oxidizing nature.

Trifluoromethanesulphonate salts are generally soluble in dipolar aprotic solvents, and conductometric studies have been performed in some solvents. In DMSO, sodium trifluoromethanesulphonate is completely dissociated as well as sodium perchlorate, thiocyanate, and tetraphenylborate (Ref. 44), while it is weakly ionized in the less basic solvent dimethyl sulphite, the dissociation constant being 1.95×10^{-2} mol dm^{-3} at 30°C (Ref. 45). The viscosity studies (Ref. 87) show that $CF_3SO_3^-$, SCN^-, and ClO_4^- are unsolvated in DMSO and have nonspherical kinetic entities in viscous flow. It is also shown that the ionic activation energy for viscous flow decreases in the order of $(i\text{-Amyl})_3BuN^+ = BPh_4^- > Na^+ > SCN^- \sim CF_3SO_3^- > ClO_4^-$. More extensive studies on the dissociation equilibria (Ref. 36 and 37) have been carried out in DMF and AN for the trifluoromethanesulphonates, *p*-toluenesulphonates, and methanesulphonates of alkali, alkaline earth, some other divalent metals [Ni(II), Cu(II), Zn(II), Pb(II), and Mn(II)], and tetraalkylammonium (Et_4N^+ and Bu_4N^+) ions. In DMF, these trifluoromethanesulphonates and perchlorates are completely dissociated, while *p*-toluenesulphonates and methanesulphonates are not: their dissociation constants being of the order of 10^{-1} to 10^{-3} mol dm^{-3}. In AN, both trifluoromethanesulphonates and perchlorates are associated to some extent, and the extent of association is larger, especially for divalent cations, for the former than for the latter. Ion association constants in AN are presented in Table 2, which shows the fact that the ion association tendency of trifluoromethanesulphonate anion toward monovalent cations is almost as weak as those of perchlorate, tetrafluoroborate, hexafluorophosphate, and tetraphenylborate anions. Limiting molar conductivities of some sulphonate ions are shown in Table 3.

TABLE 2. Ion association constants (mol^{-1} dm^3) in AN at 25°C by conductometry[a]

Cation	Anion										
	ClO_4^-				$CF_3SO_3^-$	BF_4^-	PF_6^-		BPh_4^-		
	(*b*)	(*c*)	(*d*)	(*e*)	(*b*)	(*e*)	(*e*)	(*f*)	(*d*)	(*e*)	(*g*)
Li^+	4	20			114						
Na^+	7	21	9	16	28	48	14		*	4	
K^+	8	28	13	28	27	56	21		*	2	
Rb^+	16	32	19	31	28	60	25		*	7	
Cs^+	27	35	20	34	27				2	19	
Et_4N^+	7	14			1						4
Bu_4N^+	3	12			4			1			6
	(*h*)				(*h*)						
Mg^{2+}	17				1900						
Ca^{2+}	272				4250						
Sr^{2+}	319				2050						
Ba^{2+}	482				1770						
Ni^{2+}	85				68						
Cu^{2+}	97				244						
Zn^{2+}	44				317						
Pb^{2+}	402				2280						
Mn^{2+}	103				1190						

* Completely dissociated. [a] Values for 1:1 ion-pair formation.
[b] Ref. 36. [c] Ref. 46. [d] Ref. 47. [e] Ref. 48. [f] Ref. 49. [g] Ref. 50. [h] Ref. 37.

TABLE 3. Limiting molar conductivities (S cm^2 mol^{-1}) of some sulphonate anions in dipolar aprotic solvents at 25°C[a]

Anion	DMSO	DMA	DMF	BuN	PC	AN
$CF_3SO_3^-$	21.7 22.48[b]	38.3	43.6	58.4	16.9	96.3
FSO_3^-	23.4	44.1	49.4			
$CH_3C_6H_4SO_3^-$	14.9	29.3	35.6	51.3	12.0	74.1
$CH_3SO_3^-$	18.8	36.4	44.1	58.4	15.1 15.3[c]	90.2 90[d]

[a] Ref. 17. [b] Ref. 44. [c] Ref. 24. [d] Ref. 23.

Dissociation in acetic acid

Trifluoromethanesulphonic acid is indeed one of the strongest Brönsted acids known in dipolar aprotic solvents as presented above. It is also shown by conductometry that trifluoromethanesulphonic acid is stronger than perchloric or fluorosulphuric acid in anhydrous acetic acid (Ref. 4 and 5). Recently, the dissociation equilibria of perchloric, trifluoromethanesulphonic, fluorosulphuric, *p*-toluenesulphonic, and methanesulphonic acids, and their sodium, tetraethylammonium, and tetrabutylammonium salts have been investigated in acetic acid by conductometry and potentiometry (Ref. 17). The order of magnitude of conductivities obtained is $HClO_4 > CF_3SO_3H \gg FSO_3H > CH_3C_6H_4SO_3H > CH_3SO_3H$ for acids and also for their sodium salts. On the other hand, the following order is obtained for tetraalkylammonium salts: $Et_4NCH_3SO_3 \sim Et_4NCF_3SO_3 > Et_4NCH_3C_6H_4SO_3 > Et_4NClO_4$, and $Bu_4NCH_3SO_3 > Bu_4NCH_3C_6H_4SO_3 \sim Bu_4NCF_3SO_3 > Bu_4NClO_4$. The order thus obtained may be considered to reflect the relative strength as acid or salt in this medium, and approximate dissociation constants are estimated. Dissociation constants of acids are also determined by potentiometry with chloranil - calomel and glass - calomel electrode pairs using *p*-toluenesulphonic acid as standard. Dissociation constants of acids and salts are summarized in Table 4. Obviously trifluoromethanesulphonic acid is as strong as perchloric acid in acetic acid, while fluorosulphuric, *p*-toluenesulphonic, and methanesulphonic acids are much weaker acids. The dissociation behavior of sodium and tetraalkylammonium salts is very different from that of acids, as presented in Table 4. For example, the dissociation constant of perchloric acid is 10^3 times as large as that of methanesulphonic acid, while the dissociation constant of $NaClO_4$ is only 10 times that of $NaCH_3SO_3$, and Et_4NClO_4 and Bu_4NClO_4 are slightly weaker than the corresponding methanesulphonates.

TABLE 4. pK values (K/mol dm^{-3}) of some sulphonic acids and their salts in acetic acid at 25°C by conductometry

Anion	Cation					
	H^+			Na^+	Et_4N^+	Bu_4N^+
ClO_4^-	5.12[a] 5.3[c*]	5.44[a*]	4.87[b*]	5.48[b*]	5.21[a]	5.02[a]
$CF_3SO_3^-$	5.14[a]	5.50[a*]	4.7[d]	5.61[a]	4.90[a]	4.63[a]
FSO_3^-	7.15[a]	7.31[a*]	6.1[d]			
$CH_3C_6H_4SO_3^-$		8.50[a]	8.46[b*]	6.51[a]	4.95[a]	4.63[a]
$CH_3SO_3^-$	8.58[a]	8.89[a*]		6.38[a]	4.90[a]	4.50[a]
CH_3COO^-				6.53[a] 6.58[b*]		

* Values obtained by potentiometry.

[a] Ref. 17. [b] Ref. 52. [c] Ref. 51. [d] Ref. 5.

It is well known (Ref. 51) that acetic acid is a differentiating solvent for strong acids because it is a protogenic solvent of low dielectric constant and consequently has only a limited ability to accept a proton from another proton donor. Consequently, inetrionic attractions in equation (1) will be much more important in acetic acid than in polar solvents of high dielectric constant (Ref. 33 and 51). Indeed, even strong electrolytes are incompletely dissociated into ions in acetic acid, the largest dissociation constant being of the order of 10^{-5} mol dm^{-3} (Ref. 33 and 52–54). The value of K_I is expected to decrease in the order perchlorate ~ trifluoromethanesulphonate, fluorosulphate > *p*-toluenesulphonate ~ methanesulphonate for acids and their salts on the basis of the charge densities of these anions. On the other hand, it can reasonably be considered that the value of K_D is larger for sulphonate than perchlorate because of the stronger hydrogen bonding nature of sulphonate with acetic acid molecules. Actually, as shown in Tables 1 and 4, the difference of pK_{HA} value between in acetic acid and in AN is about 3.5, 2.5, 0.5, and 0.2 (or −1.4) for $HClO_4$, CF_3SO_3H, $CH_3C_6H_4SO_3H$, and CH_3SO_3H, respectively. This fact shows that sulphonate anions, especially *p*-toluenesulphonate and methanesulphonate, are stabilized in acetic acid to greater extents than perchlorate. Thus the overall dissociation constant is dependent on K_I and K_D values as shown in equation (2), and not a good measure of acid or salt strengths. The actual strength of acids, bases or salts is reflected in the value of the ionization constant, K_I (Ref. 33 and 51). Though fluorosulphuric acid unexpectedly behaves as a weak acid in acetic acid and the detailed interpretation is not given anywhere, fluorosulphuric acid is the strongest acid in the more acidic solvent sulphuric acid (Ref. 6), as expected from the fact that the electron-withdrawing ability of fluorine attached to the sulphonyl group is stronger than that of trifluoromethyl group (Ref. 35). The order of acid strengths in sulphuric acid is as follows (Ref. 6): $FSO_3H > ClSO_3H \sim CF_3SO_3H \gg HClO_4$. The dissociation constant of trifluoromethanesulphonic acid in sulphuric acid, 8×10^{-4} mol kg^{-1}, means that the acid can donate a proton to the sulphuric acid solvent, whereas perchloric acid, though described as a very weak acid, is effectively a nonelectrolyte and methanesulphonic acid probably a base of the sulphuric acid system (Ref. 55). The fluorosulphuric acid systems are recently reviewed by Natarajan and Jache (Ref. 85), and the conductometric studies on $H_2S_2O_7$, $HClO_4$, CF_3SO_3H, and FSO_3H has been reported in trifluoroacetic acid (Ref. 86).

ELECTROCHEMICAL USE AS SUPPORTING ELECTROLYTES

Electrode reactions in non-aqueous solvents are strongly influenced by the kind of supporting electrolyte used. In choosing supporting electrolytes, several factors must be considered: solubility and electrolytic conductivity, electrochemical inertness toward oxidation and reduction, and ease of preparation and purification. Furthermore, effects on electrode reactions, of interactions between supporting electrolytes and electroactive species or electrochemical products such as ion-pair and complex formations, must be taken into account. Properties of the double layer may also be influenced by supporting electrolytes used, and electrode reactions may be remarkably changed as demonstrated in DMA and hexamethylphosphoramide (Ref. 56–59). From these points of view, tetraalkylammonium ions such as Et_4N^+ and Bu_4N^+, and alkali metal ions such as Li^+ and Na^+ have been widely used as supporting electrolyte cations, and halides such as Br^- and I^-, perchlorate, tetrafluoroborate, and hexafluorophosphate as anions. Among

TABLE 5. Solubilities and electrolytic conductivities of tetraalkylammonium salts at 25°C

Electrolyte	Solubility[a] / mol dm^{-3}			Electrolytic conductivity/ S cm^{-1}			
	DMF	AN	THF[e]	Concentration / mol dm^{-3}	DMF $\times 10^{-2}$	AN $\times 10^{-2}$	THF $\times 10^{-2}$
Et_4NClO_4[b]	1.00	1.13	<0.01	0.6	1.92	3.85	
				0.1[c]	0.538	1.08	
				0.05[c]	0.298	0.610	
Et_4NBF_4[b]	1.24	1.69	<0.01	1.0	2.63	5.56	
				0.5	1.85	3.70	
$Et_4NCF_3SO_3$[d]	2.58	3.10	0.08	1.0	2.11	4.24	
				0.5	1.59	3.06	
				0.2	0.826	1.74	
				0.1	0.488	1.04	
				0.05[c]	0.289	0.607	
$Et_4NCH_3C_6H_4SO_3$[c]				0.1	0.360	0.807	
				0.05	0.211	0.477	
$Et_4NCH_3SO_3$[c]				0.1	0.417	0.923	
				0.05	0.239	0.526	
Et_4NBr[b]	0.19	0.37	<0.01				
Bu_4NClO_4[b]	2.29	2.05	1.48	1.0			0.271
				0.6	1.30	2.70	
				0.5	1.22	2.56	0.172
				0.1[f]	0.459	0.928	
				0.05[f]	0.259	0.530	
Bu_4NBF_4[b]	2.34	2.21	2.02	1.0	1.45	3.23	0.268
				0.5	1.39	3.03	0.170
$Bu_4NCF_3SO_3$[d]	2.25	2.50	2.35	1.0	1.08	2.30	0.311
				0.5	1.12	2.25	0.209
				0.2	0.685	1.30	0.078
				0.1	0.407	0.826	0.032
				0.05[f]	0.247	0.525	
Bu_4NBr[b]	1.57	1.99	0.14	0.6	0.943	2.08	
				0.5	0.909	2.08	

[a] Values at 28°C for trifluoromethanesulphonates. [b] Ref. 68. [c] Ref. 36.
[d] Ref. 16. [e] Tetrahydrofuran. [f] Ref. 37.

TABLE 6. Limiting anodic and cathodic potentials for tetraalkylammonium salts in DMF and AN

Electrolyte	Pt electrode		Hg electrode	
	DMF	AN	DMF	AN
Et_4NClO_4	$1.14 \sim -2.51^a$	$2.1 \sim -2.4^a$	$-0.09 \sim -3.29^a$	$0.28 \sim -3.23^a$
	$1.6 \sim -2.1^b$		$0.5 \sim -3.0^b$	$0.6 \sim -2.8^b$
$Et_4NCF_3SO_3$	$1.17 \sim -2.49^a$	$2.3 \sim -2.3^a$	$-0.09 \sim -3.29^a$	$0.28 \sim -3.23^a$
	$1.8 \sim -2.2^d$	$3.0 \sim -2.5^d$	$\sim -2.65^d$	$\sim -2.8^d$
Et_4NBF_4		*	$\sim -2.72^c$	$\sim -2.70^c$
Bu_4NClO_4	$1.5 \sim -2.5^b$		$-0.08 \sim -3.43^a$	$0.28 \sim -3.23^a$
			$0.5 \sim -3.0^b$	$\sim -2.77^c$
$Bu_4NCF_3SO_3$	$1.8 \sim -2.3^d$	$3.0 \sim -2.1^d$	$-0.08 \sim -3.43^a$	$0.28 \sim -3.23^a$
			$\sim -2.8^d$	$\sim -2.7^d$
Bu_4NBF_4		*	$\sim -2.80^c$	$\sim -2.74^c$

[a] Ref. 36 and 37. Values for 0.05 mol dm^{-3} solution in V *vs.* Ag/Ag^+ (0.1 mol dm^{-3}). [b] Ref. 60. Values in V *vs.* SCE. [c] Ref. 68. Values for 0.5 mol dm^{-3} solution in V *vs.* SCE. [d] Ref. 16. Values in V *vs.* Ag/AgCl. * Following values of limiting anodic potentials have been given in AN; +2.48 for ClO_4^-, +2.91 for BF_4^-, and +3.02 V *vs.* Ag/Ag^+ (0.01 mol dm^{-3}) for PF_6^-. See Ref. 62 and 64.

these electrolytes, perchlorate salts have been considered to be most useful and almost exclusively used as supporting electrolytes in non-aqueous solvents (Ref. 60), though they are well known to be unpredictably explosive. It has also been reported (Ref. 61) that perchlorate salts are not as inert toward oxidation as they are often considered to be. Tetrafluoroborate and hexafluorophosphate have been used as supporting electrolyte anions to carry out oxidations at more anodic potentials than can be achieved with perchlorate (Ref. 62–64). As for tetrafluoroborate, however, reactions with electrochemically generated cations and cation radicals have been reported (Ref. 16, 65 and 66). Thus no literally ideal supporting electrolyte anion has yet been discovered.

Recently, trifluoromethanesulphonate salts have been introduced as supporting electrolytes (Ref. 16, 36 and 37). The salts have excellent solubilities in non-aqueous solvents and dissociate to give solutions of very high electrolytic conductivities, which are both comparable to those of perchlorates and tetrafluoroborates. The solubilities and electrolytic conductivities of some sulphonates, perchlorates, and tetrafluoroborates are presented in Table 5. The limiting anodic and cathodic potentials for trifluoromethanesulphonate solutions are essentially the same as those for perchlorates and tetrafluoroborates as shown in Table 6. In another study, the specific adsorption of trifluoromethanesulphonate anion on mercury was found to be quite similar in aqueous solutions to those of perchlorate and nitrate anions (Ref. 67). In this regard, it has also been shown (Ref. 36) that the potential - drop time curve for trifluoromethanesulphonate solutions is identical in DMF and AN to that for perchlorate, while the potentials of the electrocapillary maxima in *p*-toluenesulphonate and methanesulphonate solutions are more negative than in perchlorate.

Polarographic reductions of alkali, alkaline earth, and some transition metal (II) ions have been investigated (Ref. 36 and 37) in DMF and AN, using tetraalkylammonium trifluoromethanesulphonates, *p*-toluenesulphonates, and methanesulphonates as supporting electrolytes. In *p*-toluenesulphonate and methanesulphonate supporting electrolytes, the half-wave potentials of these metal ions are more negative than in perchlorate media, especially in AN. Trifluoromethanesulphonate supporting electrolytes behave similarly to perchlorates in DMF, while the half-wave potentials of lithium and divalent metal ions in AN are slightly more negative (20 to 30 mV) in trifluoromethanesulphonates than in perchlorates. Both *p*-toluenesulphonates and methanesulphonates are largely associated in DMF and AN. In AN, the trifluoromethanesulphonates of lithium and divalent metals are more associated than perchlorates, though all are completely dissociated in DMF. These shifts of the half-wave potentials can be explained quantitatively in terms of ion-pair formation between the metal ion to be reduced and the supporting electrolyte anion.

There is another polarographic study (Ref. 40) on trifluoromethanesulphonates of some rare earth metals in DMSO and PC. The halfwave potentials are found to be only slightly more negative than those of perchlorates. The polarographic reductions of the trifluoromethanesulphonates of Pb(II), Cd(II), and TI(I) ions have also been studied in anhydrous binary solvents of DMSO - PC by the same authors (Ref. 39).

In conclusion, trifluoromethanesulphonate anion is obviously much more advantageous than other anions in electrochemical applications, taking into account the remarkable resistance to thermal decomposition and hydrolysis, the oxidative and reductive stability, the sufficiently weak nucleophilicity, and the simple preparation, purification, and dehydration, of trifluoromethanesulphonates.

OTHER ELECTROCHEMICAL USES

Trifluoromethanesulphonic acid has been applied to potentiometric and conductometric titrations in acetic acid (Ref. 17 and 69), where perchloric acid has been almost exclusively used as a titrant (Ref. 51, 70 and 71). The titrations of some metal acetates, tetraalkylammonium *p*-toluenesulphonates, and tertiary amines with trifluoromethanesulphonic acid were found to be very similar to those with standard perchloric acid in acetic acid. Unlike perchloric acid, trifluoromethanesulphonic acid and other sulphonic acids did not form precipitates or gels in, for example, titrations of potassium hydrogen phthalate. Acid - base titrations in acetic acid have also been carried out using fluorosulphuric (Ref. 29), chlorosulphuric (Ref. 72), and aliphatic (Ref. 73) and aromatic (Ref. 73 and 74) sulphonic acids, and satisfactory results were obtained. Trifluoromethanesulphonic acid, however, is considered to be superior to perchloric and other sulphonic acids as non-aqueous titrant because of its stability and strength in wide variety of solvents combined with its non-oxidizing nature.

Recently, as a solvent for electrochemical studies, some advantages of trifluoromethanesulphonic acid over other strong acids have been clarified (Ref. 3 and 75). Due to the high acidity and other useful properties such as low freezing point [−43.53°C (Ref. 80)] and low viscosity [2.87 cP (Ref. 2), 2.97 cP (Ref. 80)] in comparison with sulphuric acid, trifluoromethanesulphonic acid is shown to be a extremely valuable solvent in the generation of cation radicals for esr spectral studies (Ref. 75). Using a gold electrode, more positive potentials can be obtained in trifluoromethanesulphonic acid than in sulphuric acid, fluorosulphuric acid, and hydrogen fluoride, and this solvent is particularly well-suited to the study of strong oxidation reactions (Ref. 3). In this regard, lactones and unsaturated cyclic ketones have been synthesized by anodic oxidation of carboxylic acids in fluorosulphuric acid (Ref. 76), and similar applications in methanesulphonic acid have also been studied (Ref. 77).

The glass electrode in AN has been calibrated (Ref. 17) in mixtures of trifluoromethanesulphonic acid and of *p*-toluenesulphonic acid with their tetraalkylammonium salts, as calibrated before by using methanesulphonates and so on (Ref. 23).

The anhydrous trifluoromethanesulphonates of potassium, zinc, barium, and cadmium have been successfully used in the study on solvation of ions (Ref. 38 and 78). Trifluoromethanesulphonate anion was found to be a stronger hydrogen-bond acceptor than perchlorate, a much weaker acceptor than chloride, and a slightly weaker acceptor than chlorate, based on the small, usually endothermic, enthalpies of transfer of this anion from water to non-aqueous solvents.

Finally, the monohydrate of trifluoromethanesulphonic acid (hydronium trifluoromethanesulphonate) has been studied as a new electrolyte for hydrocarbon-air fuel cells, and proved to be a more effective electrolyte than 85% phosphoric acid (Ref. 79). The electrochemical oxidation of propane on smooth platinum at 135°C was enhanced by a factor of 15 in trifluoromethanesulphonic acid monohydrate. At a 20°C lower temperature, the oxidation of hydrogen in the acid monohydrate was also 6 times as rapid as that in 85% phosphoric acid at 135°C. These higher oxidation rates would be explained due to lower tendencies of trifluoromethanesulphonate anion adsorption on platinum; more active sites could be available for reaction in the acid monohydrate. Recently, the practical properties of trifluoromethanesulphonic acid monohydrate as a fuel cell electrolyte have been studied in detail (Ref. 89).

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REFERENCES

1. R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.* 4228 (1954).
2. R. D. Howells and J. D. McCown, *Chem. Rev.* **77**, 69 (1977).
3. J. Verastegui, G. Durand and B. Trémillon, *J. Electroanal. Chem.* **54**, 269 (1974).
4. T. Gramstad, *Tidsskr. Kjemi, Bergvesen Met.* **19**, 62 (1959); *Chem. Abstr.* **54**, 12739e (1960).
5. A. Engelbrecht and B. M. Rode, *Monatsh. Chem.* **103**, 1315 (1972).
6. D. G. Russel and J. B. Senior, *Can. J. Chem.* **52**, 2975 (1974).
7. T. Gramstad and R. N. Haszeldine, *J. Chem. Soc.* 4069 (1957).
8. L. Fabes and T. W. Swaddle, *Can. J. Chem.* **53**, 3053 (1975) and the references therein.
9. R. L. Hansen, *J. Org. Chem.* **30**, 4322 (1965).
10. A. Streitwieser, Jr., C. L. Wilkins and E. Kiehlmann, *J. Amer. Chem. Soc.* **90**, 1598 (1968).
11. W. M. Jones and D. D. Maness, *J. Amer. Chem. Soc.* **91**, 4314 (1969).
12. A. Scott and H. Taube, *Inorg. Chem.* **10**, 62 (1971).
13. A. R. Bowen and H. Taube, *Inorg. Chem.* **13**, 2245 (1974).
14. D. K. Lavallee, C. Lavallee, J. C. Sullivan and E. Deutsch, *Inorg. Chem.* **12**, 570 (1973).
15. D. Stroupe and D. F. Shriver, *Inorg. Chem.* **13**, 2652 (1974).
16. K. Rousseau, G. C. Farrington and D. Dolphin, *J. Org. Chem.* **37**, 3968 (1972).
17. T. Fujinaga and I. Sakamoto, *J. Electroanal. Chem.* **85**, 185 (1977).
18. R. L. Benoit and C. Buisson, *Electrochim. Acta* **18**, 105 (1973).
19. C. McCallum and A. D. Pethybridge, *Electrochim. Acta* **20**, 815 (1975).
20. A. K. Mishra and K. N. Tandon, *J. Electrochem. Soc.* **121**, 91 (1974).
21. M. L'Her and J. Courtot-Coupez, *J. Electroanal. Chem.* **48**, 265 (1973).
22. R. L. Benoit, C. Buisson and G. Choux, *Can. J. Chem.* **48**, 2353 (1970).
23. I. M. Kolthoff and M. K. Chantooni, Jr., *J. Amer. Chem. Soc.* **87**, 4428 (1965).
24. K. Izutsu, I. M. Kolthoff, T. Fujinaga, M. Hattori and M. K. Chantooni, Jr., *Anal. Chem.* **49**, 503 (1977).
25. E. Roletto and A. Vanni, *Talanta* **24**, 73 (1977).
26. J. F. Coetzee and R. J. Bertozzi, *Anal. Chem.* **41**, 860 (1969); **43**, 961 (1971).
27. J. F. Coetzee and I. M. Kolthoff, *J. Amer. Chem. Soc.* **79**, 6110 (1957).
28. I. M. Kolthoff, *Anal. Chem.* **46**, 1992 (1974).
29. R. C. Paul, S. K. Vasisht, K. C. Malhotra and S. S. Pahil, *Anal. Chem.* **34**, 820 (1962).
30. I. M. Kolthoff and T. B. Reddy, *J. Electrochem. Soc.* **108**, 980 (1961).

31. M. Kinugasa, K. Kishi and S. Ikeda, *J. Phys. Chem.* **77**, 1914 (1973).
32. I. M. Kolthoff and M. K. Chantooni, Jr., *J. Amer. Chem. Soc.* **95**, 8539 (1973).
33. I. M. Kolthoff and S. Bruckenstein, *J. Amer. Chem. Soc.* **78**, 1 (1956).
34. B. G. Cox, G. R. Hedwig, A. J. Parker and D. W. Watts, *Aust. J. Chem.* **27**, 477 (1974).
35. E. A. Robinson, *Can. J. Chem.* **39**, 247 (1961).
36. T. Fujinaga and I. Sakamoto, *J. Electroanal. Chem.* **67**, 201 (1976).
37. T. Fujinaga and I. Sakamoto, *J. Electroanal. Chem.* **73**, 235 (1976).
38. G. R. Hedwig and A. J. Parker, *J. Amer. Chem. Soc.* **96**, 6589 (1974).
39. J. Massaux and G. Duyckaerts, *J. Electroanal. Chem.* **59**, 311 (1975).
40. J. Massaux and G. Duyckaerts, *Anal. Chim. Acta* **73**, 416 (1974).
41. J. Barr, R. J. Gillespie and R. C. Thompson, *Inorg. Chem.* **3**, 1149 (1964).
42. A. A. Woolf, *J. Chem. Soc. A* 355 (1967).
43. W, Reed, D. W. Secret, R. C. Thompson and P. A. Yeats, *Can. J. Chem.* **47**, 4275 (1969).
44. N. P. Yao and D. N. Bennion, *J. Electrochem. Soc.* **118**, 1097 (1971).
45. N. P. Yao, E. D'Orsay and D. N. Bennion, *J. Electrochem. Soc.* **115**, 999 (1968).
46. A. D'Aprano, M. Goffredi and R. Triolo, *J. Chem. Soc. Faraday I* 1188 (1975).
47. R. L. Kay, J. B. Hales and G. P. Cunninghum, *J. Phys. Chem.* **71**, 3925 (1967).
48. H. L. Yeager and B. Kratochvil, *Can. J. Chem.* **53**, 3448 (1975).
49. J. Eliassaf, R. M. Fuoss and J. E. Lind, Jr., *J. Phys. Chem.* **67**, 1941 (1963).
50. O. S. Berns and R. M. Fuoss, *J. Amer. Chem. Soc.* **82**, 5585 (1960).
51. A. I. Popov, *The Chemistry of Nonaqueous Solvents* (Edited by J. J. Lagowski), Vol. III, Ch. 5, Academic Press, New York (1970).
52. S. Bruckenstein and I. M. Kolthoff, *J. Amer. Chem. Soc.* **78**, 1974 (1956).
53. S. Bruckenstein and I. M. Kolthoff, *J. Amer. Chem. Soc.* **78**, 10 (1956).
54. I. M. Kolthoff and S. Bruckenstein, *J. Amer. Chem. Soc.* **79**, 1 (1957).
55. J. Barr, R. J. Gillespie and E. A. Robinson, *Can. J. Chem.* **39**, 1266 (1961).
56. K. Izutsu, S. Sakura, K. Kuroki and T. Fujinaga, *J. Electroanal. Chem.* **32**, App. 11 (1971).
57. K. Izutsu, S. Sakura and T. Fujinaga, *Bull. Chem. Soc. Japan* **45**, 445 (1972).
58. K. Izutsu, S. Sakura and T. Fujinaga, *Bull. Chem. Soc. Japan* **46**, 493 (1973).
59. K. Izutsu, S. Sakura and T. Fujinaga, *Bull. Chem. Soc. Japan* **46**, 2148 (1973).
60. C. K. Mann, *Electroanalytical Chemistry* (Edited by A. J. Bard), Vol. III, p. 57, Dekker, New York (1969).
61. C. K. Mann and K. K. Barnes, *Electrochemical Reactions in Nonaqueous Systems*, p. 509, Dekker, New York (1970).
62. M. Fleischmann and D. Pletcher, *Tetrahedron Lett.* 6255 (1968).
63. T. Osa, A. Yildiz and T. Kuwana, *J. Amer. Chem. Soc.* **91**, 3994 (1969).
64. L. C. Portis, J. C. Roberson and C. K. Mann, *Anal. Chem.* **44**, 294 (1972).
65. V. R. Koch and L. L. Miller, *J. Electroanal. Chem.* **43**, 318 (1973).
66. G. Bontempelli and R. Seeber, *J. Electroanal. Chem.* **73**, 295 (1976) and the references therein.
67. R. De Levie and J. C. Kreuser, *J. Electroanal. Chem.* **38**, 239 (1972).
68. H. O. House, E. Feng and N. P. Peet, *J. Org. Chem.* **36**, 2371 (1971).
69. E. S. Lane, *Talanta* **8**, 849 (1961).
70. J. Kucharsky and L. Safarik, *Titrations in Non-aqueous Solvents*, Elsevier, Amsterdam (1965).
71. I. Gyenes, *Titration in Nonaqueous Media*, London Iliffe Books, Princeton, N. J. (1967).
72. K. C. Mohan Rao and P. R. Naidu, *J. Electroanal. Chem.* **35**, 429 (1972).
73. S. M. M. Caso and M. Cefola, *Anal. Chim. Acta* **21**, 374 (1959).
74. D. J. Pietrzyk and J. Belisle, *Anal. Chem.* **38**, 969 (1966).
75. G. C. Yang and A. E. Pohland, *J. Phys. Chem.* **76**, 1504 (1972).
76. D. Pletcher and C. Z. Smith, *J. Chem. Soc. Perkin I* 948 (1975).
77. C. J. Myall and D. Pletcher, *J. Chem. Soc. Perkin I* 953 (1975).
78. G. R. Hedwig, D. A. Owensby and A. J. Parker, *J. Amer. Chem. Soc.* **97**, 3888 (1975).
79. A. A. Adams and H. J. Barger, Jr., *J. Electrochem. Soc.* **121**, 987 (1974).
80. R. Corkum and J. Milne, *Can. J. Chem.* **56**, 1832 (1978).
81. J. Talarmin, M. L'Her and J. Courtot-Coupez, *C. R. Acad. Sc. Paris, t. 287, série C* 105 (1978); *J. Chem. Res. (M)* 0327–0372 (1977) and (*S*), 28 (1977).
82. J. Talarmin, M. L'Her, A. Laouenan and J. Courtot-Coupez, *J. Electroanal Chem.* **103**, 203 (1979).
83. I. M. Kolthoff and M. K. Chantooni, Jr., *J. Amer. Chem. Soc.* **90**, 3320 (1968).
84. M. K. Chantooni, Jr., and I. M. Kolthoff, *J. Amer. Chem. Soc.* **92**, 2236 (1970).
85. S. Natarajan and A. W. Jache, *The Chemistry of Nonaqueous Solvents* (Edited by J. J. Lagowski), Vol. VB, Ch. 2, Academic Press, New York (1978).
86. J. B. Milne, *The Chemistry of Nonaqueous Solvents* (Edited by J. J. Lagowski), Vol. VB, Ch. 1, p. 18, Academic Press, New York (1978) and the references therein.
87. N. P. Yao and D. N. Bennion, *J. Phys. Chem.* **75**, 1727 (1971).
88. K. U. Din and P. H. Plesche, *J. Electroanal. Chem.* **93**, 29 (1978).
89. T. Sarada, R. D. Granata and R. T. Foley, *J. Electrochem. Soc.* **125**, 1899 (1978).