Dielectric Increments, Intercharge Distances and Conformation of Quaternary Ammonioalkylsulfonates and Alkoxydicyanoethenolates in Aqueous and Trifluoroethanol Solutions

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ω-(Triethylammonio)alkane-α-sulfonates $(H_5C_2)_3N^+{-}(CH_2)_n{-}SO_3^-$ (n = 2–4), pyridinio-, 2,6-lutidinio- and *N*-methylimidazolinio-propanesulfonates, and triethylammonioalkoxydicyanoethenolates $(H_5C_2)_3N^+{-}(CH_2)_n{-}O{-}CO{-}C^-(CN)_2$ (n = 2, 3) have been studied by dielectric measurements (1 MHz–1 GHz) in dilute aqueous or trifluoroethanol solution. Their intercharge distances have been derived from their dipole moments (μ in the range 18–30 D) calculated according to Buckingham's theory, and compared with the maximum and minimum intercharge distances estimated by molecular mechanics for the ideal fully extended and ion-pair conformations respectively. For identical tether length, stronger charge delocalization in the cationic (imidazolinium *versus* pyridinium) or anionic (dicyanoethenolate *versus* sulfonate) sites slightly increases the intercharge distance, while better specific solvation of the zwitterions by hydrogen bonding in the less dissociating trifluoroethanol does not result in any significant conformational change with respect to aqueous solutions. Folding of the intercharge arm, negligible for 2-(triethylammonio)ethane-1-sulfonate, progressively increases with its length, but the ion-pair conformation, where the intercharge distance becomes rapidly insensitive to the tether length, is never reached. This behaviour is in good agreement with the variations of the apparent ΔpK_a values of the zwitterions (normalized to that of $n\text{-}C_4H_9SO_3H$) measured by potentiometry in acetic anhydride–acetic acid (9:1, v/v) solution.

Since their emergence more than thirty years ago[1,2] and after a rather long period of relative oversight, stable zwitterionic polymers have recently received much attention to become a well identified class of new dipolar polymeric materials.[3] Poly(ammoniosulfobetaines) (zwitterionic lateral group $R_3N^+{-}(CH_2)_n{-}SO_3^-$, n = 2–4) for instance display a wide spectrum of unique and specific properties of basic and technological interest, including the following:

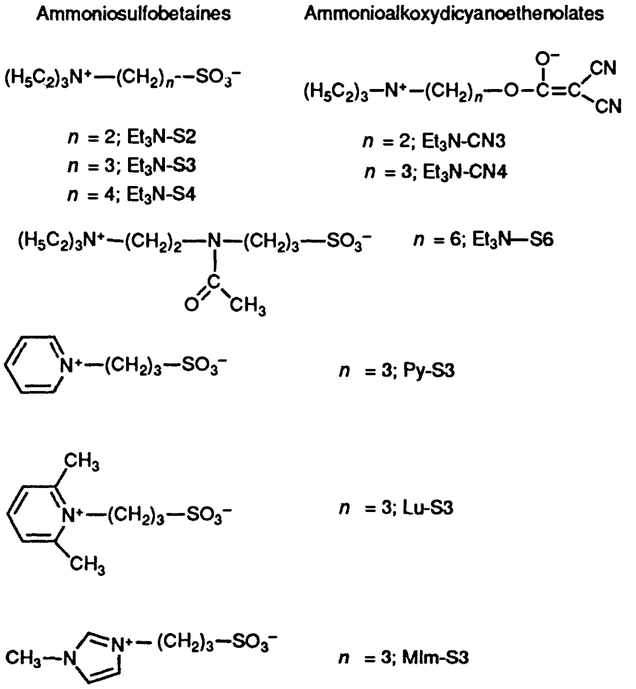
(i) 'Antipolyelectrolyte' behaviour in aqueous solution: the coil expansion of the linear chains[4–8] and the swelling of crosslinked polymers[9,10] are increasing functions of the ionic strength of the solution.

(ii) High solvation power in bulk towards a variety of mineral salts to yield amorphous ionic blends.[11–13]

(ii) Ease of polarization of thin films to yield highly dipolar electrets.[11,14]

There is no doubt that these specific properties arise from the very high local dipole typical of the zwitterionic structure and from the strong dipole–dipole or ion–dipole interactions which may occur in such systems. However reliable *experimental* values of this dipole moment still remain unknown for a number of zwitterions, although this molecular parameter definitely appears to be of outstanding importance for the derivation of quantitative structure–property correlations.

Quite recently however, intercharge distance in representative quaternary ammonium betaines (excluding amino acids) have been derived mainly from conformational analysis through NMR or molecular and quantum mechanics for the homologous series of carboxybetaines[15,16] $R_3N^+(CH_2)_nCO_2^-$ with n = 1–7 (R = CH_3[15] or long alkyl chain[16] in C_{12} or C_{16}) and of sulfobetaines[17] $R_3N^+{-}(CH_2)_n{-}SO_3^-$ with n = 1, 3 and 4 (R = hexyl). In the present work, we focus our attention mainly on the calculation of the dipole moment from dielectric measurements in polar solvents for two series of low molecular weight zwitterionic species chosen as model compounds for the corresponding polymers of current interest in our laboratory:[18,19] hydrophilic ammoniosulfobetaines studied in water and in trifluoroethanol (TFE) and hydrophobic ammonioalkoxydicyanoethenolates studied in TFE solution.



$(H_5C_2)_3N^+{-}(CH_2)_n{-}SO_3^-$

n = 2; $Et_3N\text{-}S2$
n = 3; $Et_3N\text{-}S3$
n = 4; $Et_3N\text{-}S4$

$(H_5C_2)_3{-}N^+{-}(CH_2)_n{-}O{-}C(O^-){=}C(CN)_2$

n = 2; $Et_3N\text{-}CN3$
n = 3; $Et_3N\text{-}CN4$

$(H_5C_2)_3N^+{-}(CH_2)_2{-}N(COCH_3){-}(CH_2)_3{-}SO_3^-$ n = 6; $Et_3N\text{-}S6$

n = 3; Py-S3

n = 3; Lu-S3

n = 3; MIm-S3

Critical comparison of the experimental data within these two series may afford useful information on a number of major factors controlling the characteristic zwitterion intercharge distance such as: steric hindrance and polarizability of the charged sites, length, flexibility and hydrophobicity of the tether between these charged sites, polarity of the solvent, mainly considered through its relative permittivity (ε = 78.6 and 26.7 for H_2O and TFE at 25 °C respectively). Moreover, the comparison of the experimental dipole moment values with those derived from molecular mechanics (literature or our own values) and a semi-quantitative analysis of the basicity of the anionic site (potentiometric measurements in 9:1 acetic anhydride–acetic acid), may also cast some light on the still debated topic of the preferred conformation of zwitterionic species in solution:[15,16,20] curled or ion-pair conformation (electrostatic attraction between the ionic sites) *versus* extended conformation, which depends on a complex balance between opposite contributions such as those quoted previously.

In all the following text the zwitterion is denoted by a symbol recalling its amino precursor and the nature of the anionic site followed by a figure related to the number of carbons (or heteroatom, N,O) between the charged sites: Lu-S3 stands for lutidinium-3-sulfopropylbetaine for instance.

Experimental

Physical Characterization of the Zwitterions.—Melting points (m.p.) and enthalpies (ΔH_m) were measured on a Perkin-Elmer DSC-4 differential calorimeter (heating rate of 1 °C min^{-1}, calibration with indium). ^1H NMR spectra were recorded either in D_2O (sulfobetaines) or in [$^2H_6$]dimethyl sulfoxide (cyanoethenolates) at room temperature on a Bruker AC 200 (200 MHz) spectrometer; chemical shifts, expressed in ppm, were calculated with respect to the solvent signal fixed at 4.60 and 2.49 ppm for D_2O and [$^2H_6$]DMSO respectively.

Molecular weight measurements were performed by vapour phase osmometry on a Knauer osmometer, using trifluoroethanol solutions of the zwitterions at 27 °C, after previous calibration with recrystallized benzocaine. Because of the rather low vapour pressure of the solvent at this temperature (< 100 Torr), measurements are not very reliable (continuous weak drift of the ΔR readings with no true equilibrium values), and the accuracy on the number average molecular weight of the solute is not better than ± 10%. The partial specific volume v_2 of the various zwitterions were measured at 25 °C on an Anton Paar densimeter (model 60 + 601) using aqueous and trifluoroethanol solutions for the sulfonates and the cyanoethenolates respectively: for concentrations lower than 2.5 g dl^{-1} the additivity relation $v = \Sigma_i w_i v_i$, where v_i and w_i are the partial specific volume and the weight fraction of component i, is perfectly obeyed with correlation coeffficients higher than 0.999 over five concentrations. The refractive indexes of the corresponding concentrated solutions (15–60 g dl^{-1}) were measured at 25 °C on a Abbe refractometer (λ = 589.3 nm): in all cases, the linear additivity relation[20] $n^2 = \Sigma_i \Phi_i n_i^2$, where n_i and Φ_i are the refractive index and the volume fraction of component i, is perfectly obeyed, with correlation coefficients higher than 0.999 over four concentrations; moreover, for Et_3N-S3, the experimental data obtained in H_2O and TFE lead to calculated n_2 values differing by less than 1%.

Synthesis of the Zwitterions.—Solvents and reagents. Propane and butane sultones were purified by vacuum distillation. Triethylamine, the heterocyclic amines (pyridine, lutidine, *N*-methylimidazole) and dimethylformamide (DMF) were distilled over CaH_2, and acetonitrile (ACN) over P_2O_5. 3-(2-Methyl-1,3-oxazolinio)propanesulfonate[21] and dicyano-ethylene and -propylene acetals[22] were prepared according to literature methods.

General procedure for the preparation of the sulfopropyl- and sulfobutylbetaines.[23] A solution containing 0.5 mol of propane or butane sultone and 0.55 mol of tertiary amine in 100 cm^3 of ACN was stirred under argon at 70 °C for 24 h. After cooling to room temperature, the insoluble zwitterions were separated by filtration, thoroughly washed with ACN and dried under vacuum (10^{-2} Torr) at 80 °C. They were further recrystallized from anhydrous alcohol with yields of *ca.* 80%.

Et_3N-S3: yield 89%; m.p. 284.7 °C (decomp.) ΔH_m 133 J g^{-1}. $\delta_H(D_2O)$ 3.01–3.15 [m, 8 H, $(CH_2)_4N^+$], 2.73 (t, 2 H, $CH_2SO_3^-$), 1.80–1.96 (m, 2 H, CH_2-CH_2-CH_2), 1.03 [t, 9 H, $(CH_3)_3$-CH_2N^+] (Found: C, 47.9; H, 9.5; N, 6.4; O, 22.0; S, 14.1. Calc. for $C_8H_{19}NO_3S$: C, 48.40; H, 9.48; N, 6.27; O, 21.49; S, 14.36%).

Et_3N-S4: yield 41%; m.p. 293.5 °C (decomp.); ΔH_m 149 J g^{-1}. $\delta_H(D_2O)$ 2.93–3.10 [m, 8 H, $(CH_2)_4N^+$], 2.73 (t, 2 H, $CH_2SO_3^-$), 1.56–1.60 (m, 4 H, –CH_2-CH_2CH_2-CH_2), 1.02 [t, 9 H, $(CH_2)_3$-CH_2N^+] (Found: C, 50.6; H, 9.8; N, 5.8; O, 20.5; S, 13.3. Calc. for $C_{10}H_{23}NO_3S$: 50.60; H, 9.77; N, 5.90; O, 20.22; S, 13.51%).

Py-S3: yield 85%; m.p. 274.3 °C; ΔH_m 187 J g^{-1}. $\delta_H(D_2O)$ 8.64–8.67 (d, 2 H, Pyr. *meta*), 8.31 (t, 1 H, Pyr. *para*), 7.84 (t, 2 H, Pyr. *ortho*), 4.53 (t, 2 H, N^+–CH_2), 2.75 (t, 2 H, $CH_2SO_3^-$), 2.15–2.30 (m, 2 H, CH_2-CH_2-CH_2) (Found: C, 47.85; H, 5.6; N, 6.5; O, 24.15; S, 15.7. Calc. for $C_8H_{11}NO_3S$: C, 47.75; H, 5.51; N, 6.96; O, 23.85; S, 15.93%).

Lu-S3: yield 26%; m.p. 279.1 °C (decomp.); ΔH_m 144 J g^{-1}; $\delta_H(D_2O)$: 7.93 (t, 1 H, Pyr. *para*), 7.46–7.50 (d, 2 H, Pyr. *meta*), 4.39–4.48 (m, 2 H, CH_2N^+), 2.89 (t, 2 H, $CH_2SO_3^-$), 1.97–2.12 (m, 2 H, CH_2-CH_2-CH-CH_2) (Found: C, 52.0; H, 7.15; N, 5.85; O, 22.0; S, 12.95. Calc. for $C_{10}H_{15}NO_3S$: C, 52.38; H, 6.59; N, 6.11; O, 20.94; S, 13.95%).

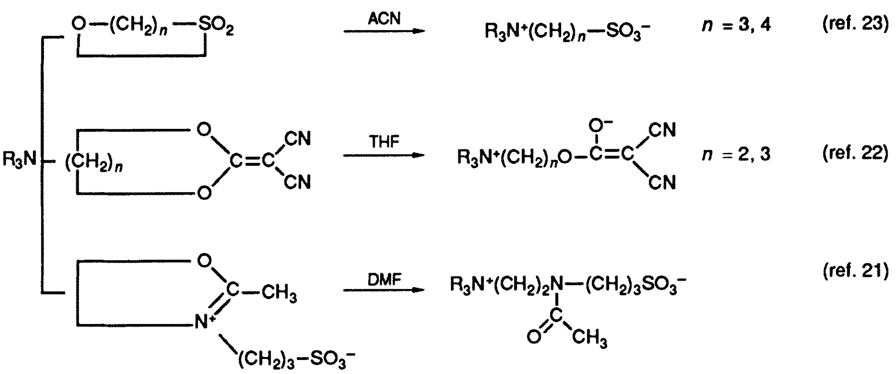
MIm-S3: yield 77%; m.p. 216.5 °C; ΔH_m 138 J g^{-1}; $\delta_H(D_2O)$ 8.53 (s, 1 H, N–CH=N^+ Im), 7.21–7.29 (d, 2 H, CH=CH Im.), 4.14 (t, 2 H, N^+–CH_2), 3.66 (s, 3 H, CH_3–N), 2.69 (t, 2 H, $CH_2SO_3^-$), 2.01–2.16 (m, 2 H, CH_2-CH_2-CH_2) (Found: C, 41.1; H, 5.95; N, 13.6; O, 23.5; S, 15.7. Calc. for $C_7H_{12}N_2O_3S$: C, 41.16; H, 5.92; N, 13.72; O, 23.50; S, 15.70%).

Et_3N-S6: A solution of 10.36 g (0.05 mol) of 3-(2-methyloxazolinio)propanesulfonate[21] and of 10.12 g (0.1 mol) of Et_3N in 50 cm^3 of DMF was heated under argon at 120 °C for 3.5 h. After cooling at room temperature, the reaction mixture was added dropwise under stirring to 400 cm^3 of dry diethyl ether (Et_2O) and the gummy yellow-orange precipitate was separated by decantation and thoroughly washed with Et_2O. After drying at room temperature under vacuum, the oil progressively crystallized on standing to give yellowish crystals which were further washed with cold chloroform ($CHCl_3$) to yield 9.6 g white crystals (yield 62%); m.p. 146.9 °C, ΔH_m 133 J g^{-1}. $\delta_H(D_2O)$ 3.27–3.52 [m, 4 H, CH_2–N($COCH_3$)–CH_2], 3.04–3.19 [m, 8 H, $(CH_2)_4$–N^+], 2.70 (t, 3 H, CH_2–SO_3^-), 1.91 (s, 3 H, CO–CH_3), 1.78–1.97 (m, 2 H, CH_2CH_2–CH_2), 1.07 [t, 9 H, $(CH_3)_3$–CH_2N^+] (Found: C, 48.25; H, 9.45; N, 8.65; O, 23.75; S, 9.85. Calc. for $C_{13}H_{28}N_2O_4S$, 0.8 H_2O: C, 48.36; H, 9.24; N, 8.68; O, 23.79; S, 9.93%).

Et_3N-S2: Triethylammonioethanesulfonate was prepared according to a literature procedure.[24] Its separation from the unreacted Na_2SO_3 and Br–C_2H_4–$N^+(C_2H_5)_3$, Br^- (see text) by selective solubilization in cold concentrated HCl did not yield a sufficiently pure product. It had to be recrystallized at least three times from isopropanol; m.p. 271.1 °C (decomp.); ΔH_m 87.1 J g^{-1}. $\delta_H(D_2O)$ 3.28–3.36 (m, 2 H, CH_2–SO_3^-), 3.05–3.16 [m, 8 H, $(CH_2)_4N^+$], 1.06 [s, 9 H, $(CH_3)_3$–CH_2N^-] (Found: C, 45.4; H, 9.35; N, 6.5; O, 22.9; S, 15.3. Calc. for $C_8H_{19}NSO_3$: C, 45.91; H, 9.15; N, 6.69; O, 22.93; S, 15.32%).

Ammonioalkoxyethenolates. They were prepared and purified by crystallization according to literature procedures.[22]

Et_3N-CN3: yield 91%; m.p. 186.9 °C (lit.,[22] 184–186 °C); ΔH_m 145 J g^{-1}. δ_H([$^2H_6$]DMSO) 4.27 (m, 2 H, CH_2–O), 3.44 (t 2 H, CH_2–CH_2N^+), 3.28 [m, 6 H, $(CH_3$–$CH_2)_3N^+$], 1.16 (t, 9 H, $(CH_3$–$CH_2)_3N^+$) (Found: C, 60.8; H, 8.25; N, 17.95; O,



Scheme 1

13.2. Calc. for $C_{12}H_{19}N_3O_2$: C, 60.74; H, 8.07; N, 17.71; O, 13.48%).

Et_3N-CN4: yield 86%; m.p. 148.4 °C; ΔH_m 123 J g^{-1}. δ_H([$^2H_6$]DMSO) 3.93 (t, 2 H, CH_2O), 3.09–3.27 (m, 8 H, $(CH_2)_4N^+$), 1.82–1.90 (m, 2 H, CH_2-CH_2-CH_2), 1.15 (t, 9 H, CH_3) (Found: C, 61.95; H, 8.45; N, 16.55; O, 13.0. Calc. for $C_{13}H_{21}N_3O_2$: C, 62.12; H, 8.42; N, 16.72; O, 12.73%).

Pyr-CN_3: yield 88%; m.p. 201.6 °C (lit.,[22] 201–202 °C); ΔH_m 121.5 J g^{-1}. δ_H([$^2H_6$]DMSO) 9.00 (d, 2 H, Pyr *ortho*) 8.62 (t, 1 H, Pyr *para*), 8.15 (t, 2 H, Pyr *meta*), 4.83 (t, 2 H, CH_2O), 4.57 (t, 2 H, CH_2N^+) (Found: C, 61.55; H, 4.15; N, 19.6; O, 15.2. Calc. for $C_{11}H_9N_3O_2$: C, 61.39; H, 4.22; N, 19.53; O, 14.87%).

Acid-base Potentiometric Measurements.—Titration of the weakly basic anionic site of the various zwitterions was performed on 6 × 10^{-3} mol dm^{-3} solutions in the binary mixture acetic anhydride–acetic acid (9:1, v/v) using a 0.1 mol dm^{-3} solution of trifluoromethanesulfonic acid in acetic acid as titrant. The Mettler DL 21 potentiometric device was fitted with a glass electrode Metrohm 6.0102.100 and a reference Ag–AgCl electrode Metrohm 6.0726.100 filled with the binary titration solvent. In our hands, and quite unexpectedly, the addition of lithium trifluoromethanesulfonate to fix the ionic strength resulted in barely detectable equivalence points, and measurements were thus performed in the absence of any electrolyte. The potentiometric curves were analysed in the usual way through the Henderson–Hasselbach equation to derive *apparent* pKa values which were normalized to that of butanesulfonic acid (chosen as reference acid) measured in identical experimental conditions (titration of n-C_4H_9-SO_3^- Na^+).

Dielectric Measurements.—Dielectric measurements were performed on aqueous or TFE solutions of the zwitterions using a Hewlett Packard impedance analyser HP 4191 A (1 MHz–1 GHz) monitored by a HP 87 computer. It allows automatic measurements of the complex permittivity $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\,\varepsilon''(\omega)$ of the solution in the whole frequency range, and may collect more than 20 data points per decade. The temperature of the measurement coaxial cell (*v ca.* 1 cm^3) was controlled to 24.2 ± 0.1 °C. The dielectric relaxation is analysed through the usual plots $\varepsilon', \varepsilon'' = F(\text{frequency } f)$.

Conformational study through Molecular Mechanics.—Three dimensional models of the zwitterions were defined using the SYBYL S.3 molecular modelling software.[25] Molecular mechanics calculations were performed with the Tripos force field including the electrostatic term.[26] Charges were calculated with the Gasteiger–Marsili algorithm in SYBYL. The formal initial positive charge was localized on the nitrogen atom. The formal initial negative charge was shared ($-\frac{1}{3}$) on each of the sulfonic acid oxygen atoms for sulfonates, while partial negative charges of −0.5 were initially ascribed to the oxygen atom and to the carbon atom carrying the two cyano substituents for the dicyanoethenolates. A systematic conformational search was performed using the SEARCH option in SYBYL with a stepwise increment of 3 to 5° for the rotatable bond dihedral angles. The curled and extended conformers, corresponding respectively to the shortest and the largest distances between the nitrogen atom and the centroid of the negative charges, were identified.

Results

Synthesis and Molecular Characterization.—All the zwitterions under study were synthesized according to known literature methods, and only some main features are outlined below. In most cases, the zwitterions were obtained through the nucleophilic ring-opening of readily available or easily prepared electrophilic reagents by tertiary amines in aprotic solvents [tetrahydrofuran (THF), acetonitrile (ACN), dimethylformamide (DMF)] according to Scheme 1.

Yields were usually higher than 60%, except for the less reactive 1,4-butanesultone (compare the yields of 41 and 89% for Et_3N-S4 and Et_3N-S3 respectively) and, as expected,[27] for the sterically hindered 2,6-lutidine (compare the yields of 26 and 85% for Lu-S3 and Py-S3 respectively).

The zwitterions generally precipitated from the reaction medium in a pure enough form, and were further recrystallized from water–ethanol solutions. Purification of Et_3N-S6 proved to be more difficult because the cyclic electrophilic reagent 2-methyl-1,3-oxazoliniopropanesulfonate[21] is already a zwitterion of similar solubility (see Experimental section). The two-step synthesis of Et_3N-S2 was based on the reaction of two salt species,[24] and required a more tedious purification procedure (see Experimental section).

$$R_3N + Br(CH_2)_2Br \longrightarrow R_3N^+(CH_2)_2Br, Br^-$$
$$\xrightarrow{SO_3Na_2} R_3N^+(CH_2)_2SO_3^- + 2\,Br^-Na^+$$

The ^1H NMR spectra are in good agreement with previous data on analogous species (see Experimental section). The most characteristic feature deals with the $CH_2SO_3^-$ resonance pattern in the homologous series of ammoniosulfobetaines. For tether length $n \geqslant 3$, it systematically appears within the narrow range 2.7–2.9 ppm as a well resolved triplet with a single coupling constant ^3J of *ca.* 6.9–7.4 Hz, which indicates free rotation around the corresponding vicinal C–C bond (CH_2–CH_2–SO_3^-). For $n = 2$ however, the $CH_2SO_3^-$ resonance pattern appears as a complex multiplet with a downfield shift of *ca.* 0.6 ppm: this behaviour may be ascribed to the deshielding effects of the closer ammonium cation and to hindered rotation of the corresponding C–C bond ($\geqslant N^+$–CH_2–CH_2–SO_3^-).

Table 1 Basicity equivalent and ΔpK_a values of the various zwitterions measured in Ac_2O–AcOH (9:1 v/v)

Zwitterion	Basic equivalent	$\Delta pK_a \pm 0.1$	Zwitterion	Basic equivalent	$\Delta pK_a \pm 0.1$
$BuSO_3^-Na^+$	1.00	0			
Et_3N-S2	—	—			
Et_3N-S3	0.993	−1.5	Et_3N–CN3	1.00	−1.7
Pyr-S3	0.974	−1.7	Pyr-CN^3	1.01	−1.9
Lu–S3	0.995	−1.5			
MIm-S3	1.00	−1.4			
DABCO-S3	1.01[a] 0.988[b]	2.8[a] −2.3[b]	DABCO–CN3	1.00[a] 0.999[b]	2.6[a] −2.1[b]
Et_3N-S4	1.00	−0.8			
Et_3N-S6	0.992	−1.1			
DMAC	0.990	−0.8			

[a] Titration of the free tertiary amino function. [b] Titration of the anionic site of the zwitterion.

Very similar features have been recently observed in a homologous series of ammoniocarboxybetaine surfactants.[16] For the methylene resonance pattern $-CH_2-O-CO-\bar{C}-(CN)_2$ in the ammoniodicyanoethenolates, a well resolved triplet at 3.93 ppm with a single coupling constant ^3J of 5.9 Hz is actually observed only in the case of Et_3N–CN4 suggesting some restriction of free rotation, at least at room temperature, for the vicinal CH_2–CH_2 bond in Et_3N–CN_3 in spite of a three atom tether $[(CH_2)_2O]$.

All the zwitterions are crystalline species showing a rather broad range of melting temperatures (140–300 °C, with higher melting points for the ammoniosulfobetaines, quite close to their decomposition temperature in most cases) but rather similar melting enthalpies (120–190 J g^{-1}). Moreover, the ammoniosulfonates are highly hygroscopic: see the 0.8 mole of tightly bound water per zwitterion for Et_3N–S6, for instance.

Finally, by analogy with some quaternization reactions,[28] some attempts to synthesize zwitterionic derivatives from 1,4-diazabicyclooctane (DABCO) with enhanced charge separation were performed according to Scheme 2.

These two successive steps may be considered respectively as the initiation (formation of species **1**) and the very beginning of the propagation (formation of species **2**) of the cationic ring-opening polymerization of DABCO.[29] In all cases the reactions carried out in a single step using a stoichiometric ratio [DABCO]/[quaternization reagent] = 2 at 25 or 60 °C failed, leading only to the monoadduct, DABCO–S3 or DABCO–CN3.

Acido–basic Properties of the Zwitterions.—The acido–basic properties of the zwitterions are of much interest with respect to their conformation in solution: the positive field arising from the quaternary ammonion cation decreases the basicity of the anionic site, and this electrostatic interaction is directly controlled by the intercharge distance.

$$R_3N^+\text{-}R'\text{-}XH \xrightleftharpoons{K_a} R_3N^+\text{-}R'\text{-}X^- + H^+$$

These effects are well-known for ammoniocarboxybetaines $[R_3N^+-(CH_2)_n-CO_2^-]$: the remarkable linear decrease of the pK_a values with the number of methylene groups between the charged sites (n = 1–10) and the good agreement of the pK_a value extrapolated to $n^{-1} \longrightarrow 0$ with that of the carboxylic acid free from any ammonium group clearly suggest that the intercharge distance increases in a monotonous way with n.[16,30]

In the zwitterions under study, the very low basicity of the sulfonate and dicyanoethenolate anions precludes any measurements in aqueous solution, and only semi-quantitative potentiometric measurements were performed in acetic anhydride–acetic-acid solution (9:1 v/v), using trifluoromethanesulfonic acid in acetic acid as titrant[18,19] (see Experimental section). The number of basic equivalents ($[CF_3SO_3H]/[R_3N^+R'X^-]$ at the equivalence point) and the *apparent* ΔpK_a values of the zwitterions defined with respect to that of butanesulfonic acid chosen as reference, $\Delta pK_a = pK_a(R_3N^+\text{–}R'\text{–}XH) - pK_a\,(BuSO_3H)$, are given in Table 1. Four main features are worth emphasizing.

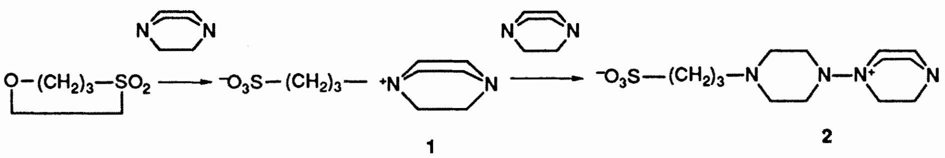
(*a*) Whenever measurable, the number of basic equivalents per zwitterion is 1.00 ± 0.01; it may be considered as a supplementary proof of the good purity of the various samples.

(*b*) For sulfonates, strong negative ΔpK_a values are observed systematically, as expected, and this effect increases when decreasing the tether length: compare for instance Et_3N–S3 and Et_3N–S4, Et_3N–S2 being too weakly basic to be titrated with our system [$\Delta pK_a \ll -2.3$, as derived from the behaviour of DABCO–S3, see further discussion (*d*)]. In the same way, for Et_3N–CN3 the ΔpK_a value previously measured in concentrated sulfuric or perchloric acid solution (40–60% by weight) with respect to sodium methyldicyanoacetate choosen as reference [same anionic site Na^+, $CH_3-O-CO-\bar{C}-(CN)_2$] is also strongly negative, *ca.* − 1.0.[19]

(*c*) For identical tether length, in terms of number of atoms, the dicyanoethenolate and sulfonate anions show rather similar basicities: compare Et_3N–S3, Pyr–S3 and DABCO–S3 with Et_3N–CN3, Pyr–CN3 and DABCO–CN3 respectively.

(*d*) With respect to Et_3N-zwitterions, the preliminary quantitative protonation of the strongly basic tertiary amine function of the homologous DABCO–zwitterions results in a supplementary charge effect which decreases further, in a significant way, the basicity of the anionic sites.

In this context, the behaviour of Et_3N–S6 remains puzzling: only one well-defined equivalence point corresponding to one basic equivalent per mole is actually observed, and it cannot be



1 **2**

Scheme 2

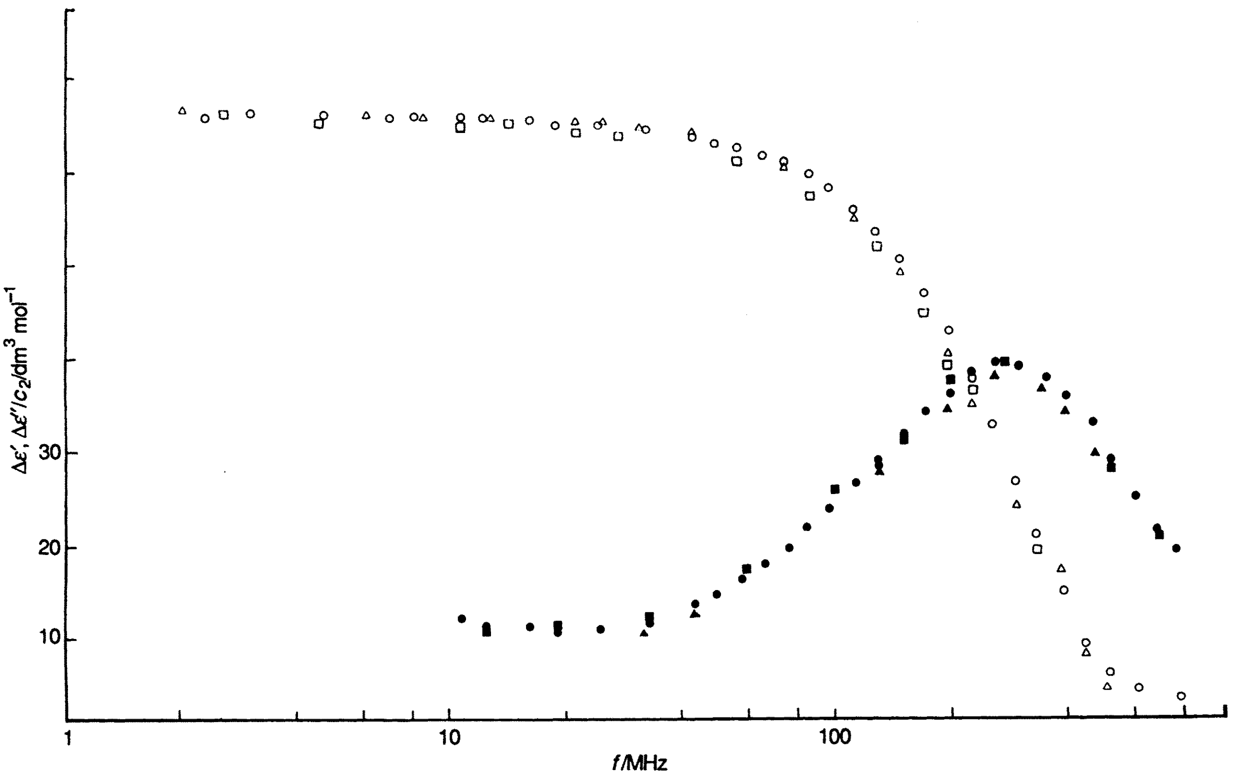
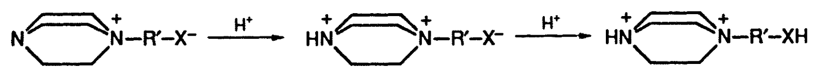


Fig. 1 Plots of $\Delta\varepsilon'/c_2$ (open symbols) and $\Delta\varepsilon''/c_2$ (filled symbols) *versus* frequency for solutions of Et_3N–S3 in TFE at 24.2 °C. c_2 = 0.045 (□), 0.090 (○), 0.213 (△), mol dm^{-3}.



unambiguously ascribed to the sulfonate or to the tertiary amide function (quantitatively titrated on a model compound such as dimethylacetamide for instance).

Finally all the above results are incompatible with any preferential intramolecular ion-pair conformation of the zwitterion in solution, as for ammoniocarboxybetaines in aqueous solution,[16,30] in spite of the significantly lower relative permittivity of the medium (ε *ca.* 19.2).

Dielectric Measurements and Data Reduction.—In all the following text, M_i, V_i, n_i and C_i are the molecular weight, the partial molar volume, the refractive index and the concentration (mol dm^{-3}) of component i in the solution. ε, n and ρ are the relative dielectric constant, the refractive index and the density of the solution. The subscripts i = 1 and 2 refer to the solvent and the zwitterionic solute respectively. T is the temperature, k Boltzmann's constant and N Avogadro's number.

Dielectric measurements in solution. Dielectric measurements were performed on a series of dilute aqueous or TFE solutions of the various zwitterions within the concentration range 0.04–0.2 mol dm^{-3}. Fig. 1 shows the variations of the increments of the static relative permittivity and dielectric loss normalized to concentration, $\Delta\varepsilon'/c_2$ and $\Delta\varepsilon''/c_2$ respectively, ($\Delta\varepsilon' = \varepsilon'_{\text{solution}} - \varepsilon'_1$ and similarly for $\Delta\varepsilon''$), *versus* frequency for Et_3N–S3/TFE solutions, chosen as a representative example. For all the concentrations, $\Delta\varepsilon'/c_2$ remains constant over a broad frequency range from 1 to 30 MHz, while both $\Delta\varepsilon'/c_2$ and $\Delta\varepsilon''/c_2$ show single dispersion centred around 270 ± 20 MHz with a slight shift towards lower frequencies on increasing concentration. The constancy of $\Delta\varepsilon'/c_2$ [regression coefficient higher than 0.999 over five data points for the linear variations $\Delta\varepsilon' = f(c_2)$] suggests that the solutions are free from any concentration dependent self-association equilibrium. In a similar way, the excellent agreement for the measured specific volumes of the zwitterion solutions with the additivity relationship $v = \Sigma_i\, w_i\, v_i$ (see Experimental section) is also in favour of aggregate free solutions. However, partial self-association of the betaines in dimers or even larger n-mers by strong dipole–dipole interactions cannot be completely ruled out *a priori*, even in a polar solvent such as TFE. Vapour phase osmometry measurements, performed on the same system Et_3N–S3/TFE at 27 °C within the concentration range 9×10^{-3}–9×10^{-2} mol dm^{-3} lead to a molecular weight of 240 ± 25 with respect to the calculated value of 223 for the isolated 'monomeric' species. The weak self-association apparently suggested by these data (*ca.* 14% of the solute aggregated into dimers for instance) cannot be well ascertained because of the low accuracy of the measurements (see Experimental section): the observed difference remains within experimental error, and the $\Delta\varepsilon'/c_2$ values may be safely identified with the molar dielectric increment at infinite dilution $(\partial\varepsilon/\partial c_2)_{c_2\to 0}$.

The relaxation times τ of the zwitterions ($\tau^{-1} = 2\,\pi\, f_c$, f_c being the critical dispersion frequency) are determined from dielectric spectra: τ = 500, 620 and 750 ps for Et_3N–S2, 3 and 4 in TFE at a common concentration of *ca.* 0.2 mol dm^{-3}, for instance. These values are close to those obtained with liquid crystals in isotropic phase.[31] For this reason, and in a first approach, the observed dielectric mechanism may be tentatively interpreted in terms of molecular rotational movements. Measurements as a function of temperature would allow a better analysis and a check of this hypothesis, but they are outside the scope of the present work.

Derivation of the solute dipole moment from dielectric *measurements in solution.* The choice of the theoretical framework for these calculations is critical when dealing with complex systems involving strongly polar and polarizable solutes in polar solvents.[15] With respect to the simple Kirkwood model for an unpolarizable point dipole[32] (currently[33] but improperly[20] used for the zwitterionic form of amino acids in aqueous solution) and to Osipov's theory, more specific to polar systems[34] but restricted to spherical molecules,[35] we prefer to adopt the more elaborate Buckingham's modification of Onsager's theory which introduces an ellipsoidal cavity for the polar and polarizable solute in a polar solvent.[36] This allows us to take into account the influence of molecular shape on the static relative permittivity of a liquid in terms of a shape factor A_i (internal field function) [eqns. (1)–(3)].

$$P = \frac{4\pi N}{9\,kT}\,\Sigma c_i\,\mu_i^2 f_i g_i^{\mathrm{B}} = \frac{(\varepsilon - n^2)(2\varepsilon + 1)}{3(2\varepsilon + n^2)} \qquad (1)$$

$$\text{where } f_i = \frac{(2\varepsilon + 1)[1 + (n_i^2 - 1)A_i]}{3[\varepsilon(1 - A_i) + n_i^2 A_i]} \qquad (2)$$

$$g_i^{\mathrm{B}} = \frac{\varepsilon[1 + (n_i^2 - 1)A_i]}{3[\varepsilon(1 - A_i) + n_i^2 A_i]} \qquad (3)$$

Buckingham's g_i^{B} factor does not correspond to Kirkwood's correlation factor g_i between the orientations of the given dipole and those of the surrounding molecules.

Straightforward differentiation of eqn. (1) with respect to c_2, leads to eqn. (4) (see below). For spherical molecules $A_i = \frac{1}{3}$, and eqn. (1) reduces to the Kirkwood–Fröhlich[37] eqn. (5) which takes into account the total field acting on the polarizable molecule,

$$P = \frac{4\pi N}{3\,kT}\,\Sigma c_i\left[g_i\mu_i^2\left(\frac{n_i^2 + 2}{3}\right)^2\right] = \frac{(\varepsilon - n^2)(2\varepsilon + n^2)}{3\varepsilon} \qquad (5)$$

where μ_i refers to the dipole moment in the gas phase.

In practice, the shape factor was calculated by assuming an extended configuration for the zwitterion,[20] and measuring on Corey–Pauling–Koltun molecular models the major axis a of the prolate ellipsoid circumscribing the molecule. The minor axis b was derived from the partial molar volume of the solute V_2 in water or TFE, depending on the solvent used in the dielectric measurements, according to: $b = (6\ V_2/N\pi a)^{0.5}$. The A_2 value was thus taken from literature compilation for the various a/b ratios.[38] Moreover, the $\partial n/\partial c_2$ term is negligible with respect to the dielectric increment one for strongly dipolar solutes. Water and TFE were assumed to be spherical in a first approach.

The major influence of the shape factor is worth emphasizing. With respect to spherical shape, the calculated μ_2 value in aqueous solution is already increased by *ca.* 16% in the most favourable case of Et_2N-S2 (less prolate ellipsoid) and by more than 50% in the most unfavourable case of Et_3N-S6 (most prolate ellipsoid). However, it has to be stressed that Buckingham's μ_2 values are obviously *maximum* values since the shape factor A_2 was calculated assuming *a priori* an extended conformation of the zwitterion: for the same Py-S3 in aqueous solution, the change from the extended to the curled conformation would decrease the μ values from 24.2 to 18.7 D, for instance. It thus clearly appears, that the data given in Tables 2 and 3 (see below) have to be considered quite cautiously, and that dielectric measurements do not lead to unique and definitely well-ascertained values of the zwitterion dipole moments which remain strongly model dependent. However, comparison of the experimental data within the framework of Buckingham's calculations may afford reliable and useful information when applied to homologous series, such as those under investigation.

Discussion

The characteristic molar dielectric increments ($\partial\varepsilon/\partial c_2$), the μ values (1 D = 3.336 × 10^{-30} C m) and the corresponding intercharge distances R [R(Å) = μ(D)/4.803] are given in Tables 2 and 3 for the various aqueous and TFE systems respectively.

Influence of Charge Delocalization and of the Polarizability of the Ionic Sites.—For the homologous series of sulfopropylbetaines (n = 3) in aqueous solution, the change from the aliphatic triethylammonium cation to the heterocyclic pyridinium or slightly more hindered 2,6-lutidinium cations does not result in any significant variation of the intercharge distance R. However, the increase of *ca.* 14% when going from the pyridinio to the *N*-methylimidazolinio betaines is consistent with the increased charge delocalization in the imidazolinium cation: this may account for the difference observed between poly(betaines) in the pyridinio and imidazolinio series with respect to their salt–polymer interactions in dilute aqueous solution.[8] Moreover triethylammoniosulfonates and dicyanoethenolates in TFE solution may be compared in a first approach ignoring any difference between a methylene group and an oxygen atom: Et_3N-S3 and Et_3N-S4 *versus* Et_3N-CN3 and Et_3N-CN4 respectively. Here again, the higher intercharge distance observed in the dicyanoethenolates may be correlated with the stronger charge delocalization in the acylated malononitrile anionic site.[22]

Influence of the Solvent.—For triethylammoniosulfobetaines (n = 2–6), the calculated μ and R values are increased by a factor in the range 1.04–1.10 when going from aqueous to TFE solutions. This weak but systematic solvent effect is more evident on the analogous variations of the molar dielectric increment $(\partial\varepsilon/\partial c_2)_{c_2 \to 0}$ which are calculation independent. A similar effect has been recently observed[15] in the homologous series $(CH_3)_3N^+$–$(CH_2)_n$–CO_2^-: the nitrogen to carboxylate distances, derived from ^{13}C NMR conformational analysis, are enhanced on going from water to methanol by a factor which increases from 1.04 for n = 4 to 1.14 for n = 7. For the systems under investigations, it is difficult to ascertain the very weak solvent effect on physically sound grounds: it may result from a complex balance between a number of solute–solvent interactions which may afford opposite contributions to the overall effect. The much higher dielectric permittivity of water (ε = 78.5 *versus* 26.7 for TFE) would result in longer intercharge distances, but stronger hydrophobic effects in water which is more self-associated than fluorinated alcohols, would favour less extended conformations of the $(CH_2)_n$ tether, especially for large n values.[15] On the other hand, if specific solvation effects on the sterically hindered tetraalkylammonium site may be safely neglected, hydrogen bonding to the anionic sulfonate site should be higher in TFE, a far better hydrogen bond donor than water: see for instance the Taft scale for hydrogen bond

$$\mu_2^2 = \frac{9\,kT}{4\pi N}\,\frac{1}{f_2\,g_2^{\mathrm{B}}}\left\{\frac{\partial\varepsilon/\partial c_2[4\,\varepsilon_1(\varepsilon_1 - n_1^2) + n_1^2\,(3 - 2\,n_1^2)] - 6\,\partial n/\partial c_2\,\varepsilon_1\,n_1(1 + 2\,\varepsilon_1)}{3(2\varepsilon_1 + n_1^2)^2}\right\} + \frac{\mu_1^2}{V_1 f_2 g_2^{\mathrm{B}}}\,[(V_2 f_1 g_1^{\mathrm{B}}(\partial f_1/\partial c_2)g_1^{\mathrm{B}} - f_1(\partial g_1^{\mathrm{B}}/\partial c_2)] \qquad (4)$$

Table 2 Specific volumes, refractive indices, dielectric increments, shape-factors, dipole moments and intercharge distances for the zwitterions in aqueous solution

Zwitterion	v_2/cm^3 mol^{-1}	n_2	$(\delta\varepsilon/\delta c_2)_{c_2 \to 0}$/dm^3 mol^{-1}	A_2	μ_2/D	R/Å
Et_3N-S2	0.7841	1.5016	42.2	0.265	18.7	3.90
Et_3N-S3	0.8174	1.5083	58.6	0.240	23.0	4.80
Et_3N-S4	0.8330	1.5131	75.4	0.210	27.6	5.75
Et_3N-S6	0.812	1.5736	72.9	0.155	30.3	6.30
MIm-S3	0.7152	1.5310	60.9	0.160	27.5	5.75
Pyr-S3	0.7042	1.5730	57.5	0.195	24.2	5.05
Lu-S3	0.7599	1.5609	60.3	0.215	23.9	5.00

Table 3 Specific volumes, dielectric increments, shape-factors, dipole moments and intercharge distances for the various zwitterions in TFE solution. R_c and R_e: intercharge distance calculated for the fully extended and the curled conformation respectively

					Intercharge distance RzÅ		
Zwitterion	v_2/cm^3 mol^{-1}	$(\delta\varepsilon/\delta c_2)_{c_2 \to 0}$/dm^3 mol^{-1}	A_2	μ_2/D	R	R_c	R_e
Et_3N-S2	0.7375	44.9	0.260	20.5	4.30	3.55	4.34
Et_3N-S3	0.7558	65.3	0.230	24.0	5.00	4.28	5.62
Et_3N-S4	0.7623	87.0	0.200	29.7	6.20	4.30	7.02
Et_3N-S6	0.7490	80.4	0.145	31.6	6.60	4.30	9.59
MIm-S3	0.6276	66.2	0.150	28.7	6.00		
Pyr-S3	0.6140					3.18	6.02
Et_3N-CN3	0.8282	65.5	0.195	25.9	5.40	4.30	6.02
Et_3N-CN4	0.8410	81.7	0.170	30.8	6.40	4.30	7.34

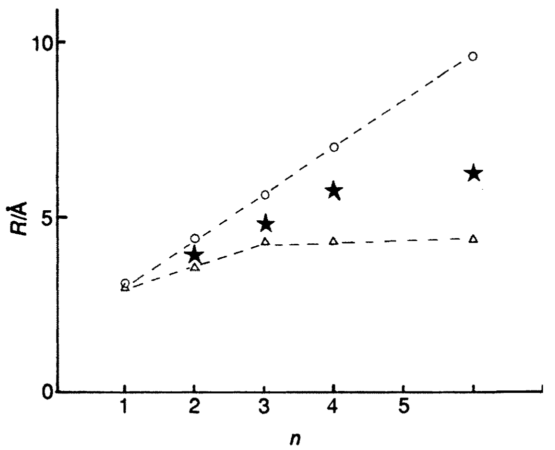


Fig. 2 Variations of the intercharge distance R(Å) for the triethylammonioalkylsulfonates in TFE solution with the tether length n. R_e (○) and R_c (△): calculated values for the fully extended and curled conformations respectively.

donating power of solvents,[39] and the strongly negative Gibbs energy of transfer for a variety of anions from water to TFE.[40]

All these factors are probably involved in the decrease of the partial molar volume V_2 of the zwitterions when transferred from water to TFE: this contraction of *ca.* 6–12%, definitely out of the error domain (the accuracy on V_2 is much better than 1%, see Experimental section), may appear rather high and is consistent with stronger solute–solvent interactions in TFE. However, any important conformational change when transferring the zwitterions from one solvent to the other may be reasonably ruled out.

Influence of the Tether Length on the Conformation of the Zwitterions in Solution.—The minimum and maximum intercharge distances R_c and R_e, corresponding to the curled and extended conformations, were calculated by Molecular Mechanics (see Experimental section) and are given in Table 3. The good agreement observed between the R_c and R_e values obtained for Et_3N-S3 (R_c = 4.28 Å, R_e = 5.62 Å) and those previously reported for [(dimethylhexylammonio)propyl] sulfonate[17] (R_c = 4.31 Å, R_e = 5.77 Å) may be considered as a positive check of the reliability of our calculations.

The variations of the intercharge distance R with the length of the tether chain n for the sulfonate zwitterions in trifluoroethanol solution are plotted in Fig. 2 and the corresponding values for aqueous solutions are compared with some closely related literature data for H_3N^+-$(CH_2)_n$-SO_3^- (n = 2 and 3, dielectric measurements in aqueous solution and calculations according to the same Buckingham's equations[20]) and for $(CH_3)_3N^+$-$(CH_2)_n$-CO_2^- (n = 2–7, nitrogen–carboxylate distances derived from ^{13}C NMR conformational analysis[15]) in Table 4. With respect to the well defined linear increase of the R values with the tether length n for the carboxybetaines,[15] fairly parallel variations may be observed for the other zwitterionic species within homologous series (constant anionic and cationic sites) for $n \leqslant 4$. This trend, which should be confirmed more especially on sulfobetaines with $n > 4$, is rather gratifying, and the slight differences observed at constant n are probably related to the structural differences of the charged sites: the order of increasing R values, carboxylate < sulfonate < dicyanoethenolate, may be tentatively correlated with the increased charge delocalization in the anionic site (a slight enhancement due to solvent effects may also be involved for dicyanoethenolates in TFE solution, see above). Et_3N-S6 clearly stands out of the previous correlation, but the influence of its central bulky tertiary amide function with strong hydrogen bond accepting power should differ from that of a methylene group.

The linear increase $\mu \propto n$ is more in favour of an extended conformation than a curled one, and the intercharge distance R calculated from the dielectric measurements has been compared to the maximum intercharge distance for the fully extended conformation, R_e, derived from molecular mechanics (ideal isolated zwitterion in the gas phase). The variations of the ratio $r = R/R_e$ with the tether length for the same zwitterionic species are plotted in Fig. 3. Here again a common general trend clearly appears, whatever the structure of the anionic site. For n = 2, the zwitterion is practically in its fully extended

Table 4 Variations of the intercharge distance R (Å) with the tether length n for various ammonioalkanesulfonates and -alkoxydicyanoethenolates in aqueous and TFE solutions respectively

Zwitterion		n 2	3	4	5	6	7
$(CH_3)_3N^+$-$(CH_2)_n$-CO_2^-	ref. 15	3.81	4.50	5.40	6.15		7.70
H_3N^+-$(CH_2)_n$-SO_3^-	ref. 20	4.20	5.13				
Et_3N-S2 to S6	this work	3.90	4.80	5.75		6.31	
Et_3N-CN3 and 4	this work		5.40	6.42			

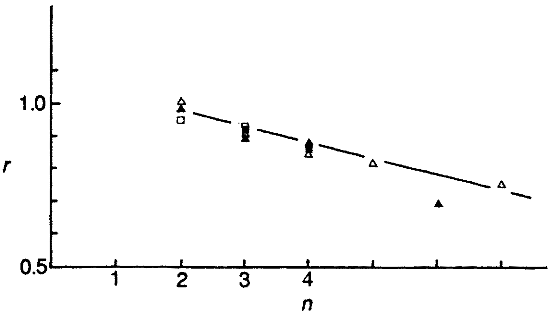


Fig. 3 Variations of the degree of folding of the intercharge arm $r = R/R_c$ with the tether length n: □, N^+H_3-$(CH_2)_n$-SO_3^- (ref. 20); ▲, $(C_2H_5)_3N^+$-$(CH_2)_n$-SO_3^-; △, $(CH_3)_3N^+$-$(CH_2)_n$-CO_2^- (ref. 15); ■, $(C_2H_5)_3N^+$-$(CH_2)_n$-O-CO-$\bar{C}$-$(CN)_2$

conformation: the short tether has no possibility of coiling. For $n \geqslant 3$, coiling becomes possible, and the characteristic ratio r is a quasi-linear decreasing function of the tether length n, except for Et_3N-S6. Because of the assumptions involved in the calculations of the intercharge distances R_c (see Experimental section) and more especially R, the values of the ratio r may be biased: they are minimum values (see calculation of R). The extent of folding of the tether is probably underestimated, but its increase with n is physically well ascertained. This typical behaviour is consistent with the development of electrostatic attractive interactions between the oppositely charged sites, even in solvent of medium or high dielectric permittivity, provided the intercharge arm shows sufficient length and flexibility. Completely curled conformation may be safely ruled out: for Py-S3 for instance, Buckingham's calculations assuming the less prolate ellipsoidal shape for the solute lead to an intercharge distance of 3.90 Å, which shows an increased coiling of the tether ($r = 0.70$) but which is still significantly higher than the R_c minimum of 3.18 Å corresponding to the ion-pair conformation. Moreover the experimental variations of R with the tether length are not compatible with the quasi-insensitivity of the calculated intercharge distance in the case of the ion-pair conformation: see Fig. 2 and Table 3.

Conclusions

For zwitterions of the ammonioalkanesulfonate or ammonioalkoxydicyanoethenolate type, an increase in the tether length results in an increased basicity of the anionic site, as derived from potentiometric measurements in acetic anhydride–acetic acid solution, and in an increased intercharge distance, as derived from dielectric measurements in aqueous or trifluoroethanol solution: these self-consistent characteristic features, similar to those already observed on analogous carboxybetaines in aqueous solution,[15,16,20,30] exclude any intramolecular ion-pair conformation in solution, even if the extent of folding of the intercharge arm increases with its length.

On the other hand, there is no doubt that in the gas phase the curled conformation is the more stable because of electrostatic interactions between the opposite charges:[15–17] the energy differences calculated by molecular mechanics are *ca.* 6.3 and 7.0 kcal mol^{-1} for (ammoniopropyl) and (ammoniobutyl) sulfonates respectively[17] in favour of the curled conformation.* This feature stresses the importance of the screening effects of the solvent which arise from its dielectric permittivity[15,16] and also from potential specific interactions (see trifluoroethanol and acetic anhydride–acetic acid solvents of much lower relative permittivity than water). Direct observation of the curled conformation favoured in non-polar media (alkanes, carbon tetrachloride) appears highly speculative: zwitterions are generally insoluble in these solvents, and, moreover, for the most soluble species such as zwitterionic amphiphilic molecules, dipolar interactions should promote their self-association in dimers or larger aggregates which involve the extended conformation.[17] 3-[4-(4-Methylthiostyryl)pyridinio]propylsulfonate, recently analysed in the crystalline state, shows an extended conformation of its zwitterionic function.[41] To the best of our knowledge, a conformational equilibrium between curled and extended conformations has been actually observed only in the case of amorphous glassy poly[4-vinylpyridinio)-propylsulfonate] previously polarized and then studied by thermally stimulated depolarization currents.[14]

Acknowledgements

The authors are greatly indebted to Dr. M. F. Hibert (Merrell Dow Research Institute, Strasbourg, France) for the molecular mechanics calculations. They acknowledge Mrs. H. Bellissent and S. Lepilliet for their efficient technical assistance.

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* 1 cal = 4.184 J.

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Paper 2/04493E
Received 20*th August* 1992
Accepted 2*nd November* 1992