

Poly(ammonio alkoxydicyanoethenolate)s as new hydrophobic and highly dipolar polyzwitterions: 3. Solubility properties

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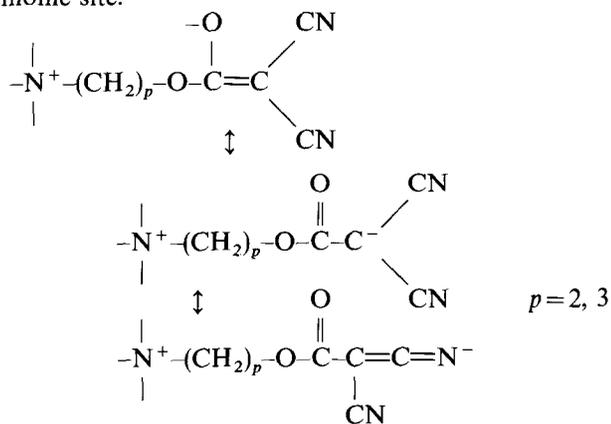
(Received 5 April 1993; revised 16 August 1993)

The solubility properties of amorphous poly[2,2-dicyano-1-[2-(2-(methacryloyloxy)ethyl)dimethylammonio]-ethoxy]-ethenolate] (zwitterionic lateral group of $\mu = 25.9$ D) investigated in 43 solvents of widely differing polarity may be interpreted in terms of solvent molar refractivity (dispersion interactions), dipole moment (dipolar interactions), basicity (donor-acceptor interactions with the ammonium site) and hydrogen-bond-donating power (hydrogen bonding to the anionic site). In dimethylformamide, representative of strongly dipolar aprotic media, the phase diagram is characterized by a lower critical solution temperature corresponding to a lower θ temperature of about $65.8 \pm 1^\circ\text{C}$. Coil expansion at 25°C , as derived from intrinsic viscosity measurements, is an increasing function of the concentration of added lithium salts ($\leq 1.5 \text{ mol l}^{-1}$), and the order of anion efficiency is $\text{Cl}^- > \text{Br}^- > \text{I}^- > \text{ClO}_4^-$. In trifluoroethanol, representative of weakly associated and strongly protic solvents, the addition of tetramethylammonium salts ($\leq 1 \text{ mol l}^{-1}$) results in coil expansion only in the case of the more polarizable ClO_4^- and I^- anions, while Cl^- and Br^- promote chain collapse. The hydrophobic polyzwitterion becomes water soluble at 25°C only in the presence of high salt concentrations, such as $\text{NaSCN} > 2.5 \text{ mol l}^{-1}$, $\text{ZnCl}_2 > 5 \text{ mol l}^{-1}$, $\text{C}_2\text{H}_5\text{NH}_3^+\text{NO}_3^- > 6 \text{ mol l}^{-1}$, and the phase diagram is characterized by an upper critical solution temperature strongly dependent on salt concentration ($dT/d[\text{NaSCN}] = -70^\circ\text{C l mol}^{-1}$). In strongly acidic media, such as concentrated H_2SO_4 , HClO_4 aqueous solution (40–60 wt%) or methanesulfonic acid, partial protonation of the anionic sites transforms the polyzwitterion into a water soluble cationic polyelectrolyte.

(Keywords: polyzwitterion; solubility properties; temperature effects)

INTRODUCTION

In two previous papers we presented an overview of the synthesis¹ of a series of amorphous atactic poly(ammonio alkoxydicyanoethenolate)s of high molecular weight, and a mechanistic analysis of the radical polymerization of the corresponding monomers². The stable zwitterionic structure of the lateral group is essentially characterized by very high dipole moments ($\mu = 25.9$ and 30.8 D, as measured for triethylammonio ethoxy and propoxydicyanoethenolates in trifluoroethanol solution³) and by a rather strongly reduced hydrophilicity resulting from the highly delocalized acyl malonitrile structure of the anionic site:



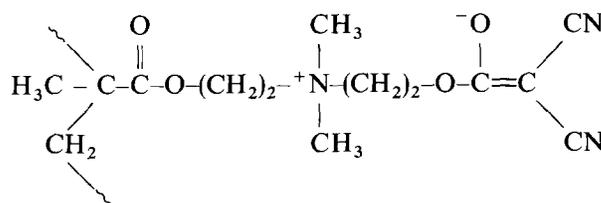
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0032-3861/94/07/1462-11

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1462 POLYMER Volume 35 Number 7 1994

The purpose of the present work is to critically discuss the solubility properties of poly[2,2-dicyano-1-[2-(2-(methacryloyloxy)ethyl)dimethylammonio]-ethoxy]-ethenolate], chosen as a representative polymer of these new polyzwitterions:



These solubility properties were studied in a wide variety of solvents with two main goals.

1. To search for functional classes of solvents for the establishment of a solubility map of the polymer, and for the semiquantitative analysis of the chain expansion in dilute solution in terms of non-specific and specific polymer-solvent interactions.
2. To analyse salt effects on the solubility properties of the polymer in different media: dimethylformamide (DMF) as representative of dipolar aprotic solvents; trifluoroethanol as representative of weakly self-associated protic solvents; and water as a unique amphiprotic, highly structured medium.

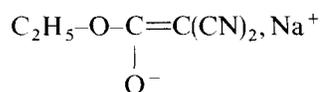
Because of their relatively broad range of solubility, poly(ammonio alkoxydicyanoethenolate)s deserve special

attention. As versatile model compounds they are of interest for at least two complementary reasons. First, it is of interest to compare them with more classical polyzwitterions, such as poly(ammonium sulfoalkylbetaines), which essentially show solubility in aqueous salt solutions characterized by a very typical 'antipolyelectrolyte' behaviour⁴⁻¹⁰ (increasing chain expansion when increasing the ionic strength). Second, of more general interest is the study of extremely polar polymer-organic solvent systems with special emphasis on salt effects. With respect to the huge literature devoted to 'salting in' and 'salting out' phenomena in aqueous polymer solutions¹¹, only a modest number of studies have addressed the effects for ternary polar organic systems, which are undoubtedly of interest from both basic and technological viewpoints; see, for instance, the critical influence of some mineral salts on the solubility properties of aliphatic and aromatic polyamides in alcohols¹² and in dipolar aprotic solvents¹³, respectively.

EXPERIMENTAL

Solvents, salts and polymers

All the dipolar aprotic solvents were purified by vacuum distillation over CaH₂ and stored over freshly regenerated 4 Å molecular sieves. Fluorinated alcohols were purified according to literature methods^{14,15}. The various alkali metal and tetramethylammonium salts of the best reagent grade were used without further purification after drying under vacuum (10⁻² torr) at 120 and 80°C, respectively. Ethylammonium nitrate was synthesized according to the literature method¹⁶: in our case, the liquid salt dried at 70°C under vacuum (10⁻² torr) contained about 500 ppm of water, as derived from Karl-Fisher titration. The polyzwitterion samples were obtained by free-radical polymerization of the corresponding monomer and characterized (light scattering measurements in DMF solution) as previously described¹. The synthesis of the cationic polyelectrolyte, poly[(methacryloyloxyethyltrimethylammonium)ethyl-dicyanoacetate], rests upon the radical polymerization of its monomer obtained by ion exchange between methacryloyloxyethyltrimethylammonium chloride and the sodium salt of ethyldicyanoacetate¹⁷:



All the studies were performed using a series of atactic unfractionated ($M_w/M_n \approx 2$) samples of different molecular weights, as given in Table 1.

Solubility tests and cloud point measurements (T_c)

These tests and measurements were performed at a concentration of 1 g dl⁻¹ on finely ground samples

Table 1 Molecular weights of samples

Sample	P.I	P.II	P.III	P.IV	P.V
$M_w \times 10^{-6}$	2.80	2.14	1.40	0.44	0.22

thoroughly dried for at least 16 h at 60°C under vacuum (10⁻² torr). When solubilization was not achieved within 5 h at room temperature, the dispersion was kept under gentle stirring for 5 h, first at 60°C and then at 5°C if heating proved to be inefficient. Cloud point measurements were carried out according to two procedures, depending on the solvent used. For aqueous salt solution, the critical minimum salt concentration (CSC) required to promote water solubility at 25°C was measured by titration of polymer solutions (2 g dl⁻¹), at high enough salt concentration, with pure water in a double-walled cell maintained by thermostat at 25°C. The accuracy of the CSC values, obtained by visual determination of the first cloud point, was about $\pm 2\%$. For DMF solution, the lower critical solution temperatures (LCSTs) were measured for polymer concentrations in the range of 1-20 wt% on a Mettler FP 80 apparatus (sealed capillary tubes) using a heating rate of 1 K min⁻¹; reproducibility of the measurements was ± 1 K. However, for polymer concentrations lower than 1 wt%, the previous experimental device does not lead to reliable measurement. In this case, the solution and a thermometer were placed directly in a test tube heated at a rate less than 5 K min⁻¹ in an oil bath; the first cloud point was obtained upon heating by visual determination with an accuracy of about ± 1 K. The transition temperature from a cloudy to a transparent solution observed upon slow cooling generally agrees with the previous value to within ± 2 K. The cloudy-clear and clear-cloudy points observed upon heating and cooling, respectively, (upper critical solution temperatures, UCST) for 1 wt% solution of the polyzwitterion in aqueous salt solution were determined in the same way.

Viscosity and density measurements

Viscosity measurements were carried out on a home-built automatic device (Ubbelohde type) at 25°C on solutions previously annealed overnight at room temperature. The intrinsic viscosity ($[\eta]$, dl g⁻¹), and the Huggins constant (K'_H) were calculated according to Sakai's procedure¹⁸ (average of the Huggins and Schulz-Blaschke extrapolations), which is expected to lead to the most reliable K'_H values for poor and moderately good solvents. The partial specific volume, v , of the polyzwitterion in DMF solution was measured on an Anton Paar densimeter (model 60+601) between 25 and 55°C: v (ml g⁻¹) = 0.7412 - 2.9 $\times 10^{-4}$ t (°C). Conversion of polymer weight fraction into volume fraction in the binary solutions was performed assuming simple additivity of the volumes of both components over the whole ranges of composition and temperature.

Spectroscopic measurements

The Dimroth-Reichardt betaine dye [2,6-diphenyl-4(2,4,6-triphenylpyridinium-1-yl)phenolate inner salt] was previously dried at 90°C under 10⁻² torr. Its u.v.-visible spectrum was recorded in DMF solution (concentration (0.18-2.4) $\times 10^{-3}$ mol l⁻¹) in the presence of various amounts of salt at room temperature on a Cary spectrometer 2300 at a scanning rate of 0.02 nm s⁻¹. Because of the very high sensitivity of the long wavelength transition of the betaine towards moisture, the accuracy on the λ_{max} value was not better than ± 0.4 nm.

RESULTS AND DISCUSSION

Solubility map of poly(ammonio ethoxydicyanoethenolate)

The solubility tests between 5 and 60°C were carried out on polymer P.III at a concentration of 1 g dl⁻¹, which is of the order of, or higher than, the critical coil overlap concentration, *C*^{*}, for all the solvents involved. They are representative of semidilute solutions only, since solubility may be a complex function of concentration in the case of polyzwitterions; see poly[1,1-dimethyl-1-(2-methacryloyloxyethyl)-1-(3-sulfopropyl)ammonium betaine] in aqueous solution^{8,19}, for instance.

Because of the very high polarity of the systems under study, instead of relying on the popular solubility parameter concept, we prefer to set up and analyse the solubility map of the polyzwitterion in terms of non-specific and specific polymer-solvent interactions, using a hybrid series of four solvent polarity descriptors:

1. the molar refractivity, $MR = V[(n_D^2 - 1)/(n_D^2 + 2)]$ (where n_D and V are the refractive index and the molar volume of the solvent, respectively), which is directly related to dispersion and Debye dipole-induced dipole interactions;
2. the dipole moment, μ , related to Keesom dipole-dipole interactions;
3. $-\Delta H_{BF_3}^0$, the negative enthalpy of complex formation of boron trifluoride with the solvent in dichloromethane solution²⁰. This recently introduced basicity scale has been shown to be more reliable than the Gutmann 'donicity' and provides a polarity parameter of interest for potential specific donor-acceptor interactions at the cationic ammonium site;
4. α , the solvatochromic hydrogen-bond-donating power of the solvent according to Kamlet *et al.*²¹; this

parameter is preferred to the well known Dimroth-Reichardt E_T scale or to the Gutmann acceptor number since the latter two also involve a dipolar contribution. The parameter α is relevant to the potential specific hydrogen bond interaction with the anionic site of the zwitterion.

The physical constants (μ , n_D , etc.) of the solvents were taken from literature compilations²²⁻²⁴ and the various empirical polarity parameters ($-\Delta H_{BF_3}^0$, α) directly from original reports (refs 20 and 21, respectively).

The solubility properties of the polyzwitterion are best analysed by considering separately dipolar aprotic solvents, organic protic solvents and finally aqueous acid or salt solutions.

Dipolar aprotic solvents ($\alpha = 0$). The experimental data given in Table 2, where every solvent is identified by a number, allow us to set up a semiquantitative three-dimensional solubility map emphasizing the relative influence of the MR , μ and $-\Delta H_{BF_3}^0$ polarity parameters. The transition between solubility and insolubility is roughly defined by the borderline solvents leading most often only to swelling effects or to gel-like solutions at room temperature. Figure 1 shows solubility domains as projections on two-dimensional maps and an optimized and rather restricted volume of high solubility.

For solvents of low or moderate basicity ($-\Delta H_{BF_3}^0 < 80$ kJ mol⁻¹), a high dipole moment ($\mu > 4$ D), even associated with a high polarizability as in the aromatic series, provides only borderline solvents (e.g. nos 14, 15, 21, 26 and 27). However, a high basicity alone, as in pyridine, does not promote solubility. The simultaneous contributions of a high dipole moment ($\mu > 3.8$ D) and a high basicity ($-\Delta H_{BF_3}^0 > 80$ kJ mol⁻¹) generally afford

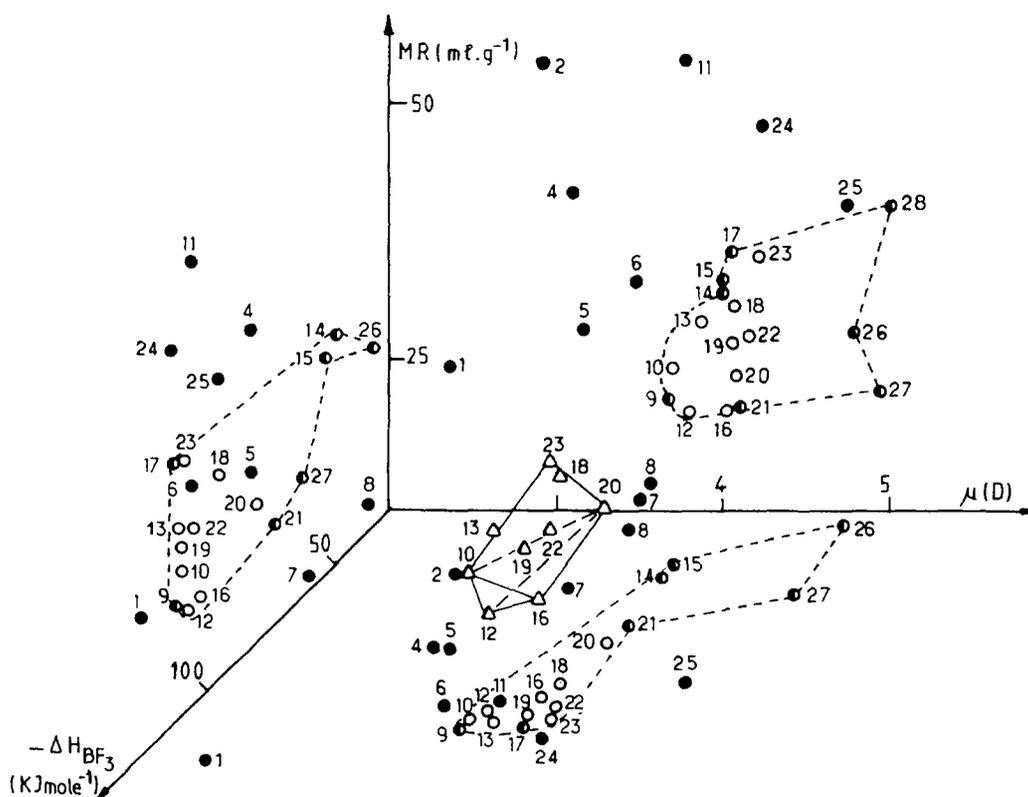


Figure 1 Three-dimensional solubility map of polyzwitterion P.III in dipolar aprotic solvents at room temperature: ○, soluble; ●, insoluble; ◐, swollen; ---, boundaries of solubility regions in two-dimensional maps; △, volume of optimum solubility in the three-dimensional map

Table 2 Solubility properties, intrinsic viscosities, $[\eta]$, and Huggins constants, K'_H , of polyzwitterion P.III ($M_w = 1.4 \times 10^6$) at 25°C, in dipolar aprotic and in protic solvents

Dipolar aprotic solvents	μ (D)	$-\Delta H_{BF_3}^0$ (kJ mol ⁻¹)	MR (ml g ⁻¹)	Solvent power ^a	$[\eta]$ (dl g ⁻¹)	K'_H
1 Pyridine	2.37	128.08	24.1	—		
2 Tetraethylsulfamide	2.80	55.08	54.2	—		
3 Methylmethyl phosphonate	2.88	92.60	27.0	—		
4 Triethylphosphate	3.12	84.75	41.8	—		
5 Trimethylphosphate	3.18	84.75	27.8	—		
6 Tetramethylurea	3.50	108.62	32.4	—		
7 Acetonitrile	3.53	60.39	11.1	—		
8 Nitromethane	3.57	37.63	12.5	—		
9 <i>N,N'</i> -diethylacetamide	3.70	113.61	21.1	+/-		
10 <i>N,N'</i> -dimethylacetamide	3.72	112.14	24.3	+	0.60	0.35
11 Dibutylsulfoxide	3.80	107.60	54.1	—		
12 <i>N,N'</i> -dimethylformamide	3.88	110.49	19.9	+	0.70	0.23
13 <i>N,N'</i> -diethylformamide	3.90	113.20	28.9	+/-		
14 Benzonitrile	4.02	55.44	31.6	+/-		
15 Nitrobenzene	4.03	35.79	32.7	+/-		
16 Dimethylsulfoxide	4.05	105.34	20.2	+	0.91	0.24
17 1-Acetylpiperidine	4.07	114.16	35.7	+/-		
18 <i>N,N'</i> -dimethylethyleneurea	4.08	98.93	30.3	+	1.35	
19 <i>N</i> -methylpyrrolidone	4.08	112.56	26.8	+	0.96	0.10
20 3-Methyl-2-oxazolidinone	4.11	83.00	23.4	+	0.88	0.21
21 γ -Butyrolactone	4.12	75.13	19.9	+/-		
22 Tetramethylene sulfoxide	4.17	108.10	27.3	+	1.58	0.15
23 <i>N,N'</i> -dimethylpropyleneurea	4.23	112.13	34.9	+	2.22	0.16
24 Hexamethylphosphoramide	4.30	117.53	47.9	—		
25 Tetramethylmethylphosphonic acid diamide	4.80	98.50	40.1	—		
26 Tetramethylene sulfone	4.81	51.32	27.2	+/-		
27 Propylenecarbonate	4.95	64.19	21.5	+/-		
28 <i>o</i> -Nitroanisole	4.98	—	39.5	+/-		
Protic solvents	μ (D)	α	MR (ml g ⁻¹)	Solvent power ^a	$[\eta]$ (dl g ⁻¹)	K'_H
1 <i>m</i> -Cresol	1.57	1.10	33.0	+	1.08	0.30
2 <i>n</i> -Propanol	1.65	0.78	17.6	—		
3 Methanol	1.71	0.93	8.2	—		
4 Ethanol	1.74	0.83	12.9	—		
5 <i>n</i> -Butanol	1.75	0.79	22.1	—		
6 Water	1.77	1.17	3.7	—		
7 Formic acid	1.82	—	8.6	+		
8 2-Chloroethanol	1.88	0.89	7.4	—		
9 Tetrafluoropropanol	1.99	1.47	17.6	+	1.05	0.28
10 Trifluoroethanol	2.03	1.51	13.2	+	1.12	0.26
11 Trichloroethanol	2.04	0.86	27.7	+/-		
12 Hexafluoroisopropanol	2.05	1.96	18.0	+	1.46	0.16
13 Ethylene glycol	2.31	0.90	14.4	—		
14 Glycerol	2.56	0.91	20.5	—		
15 Formamide	3.37	0.71	10.6	—		

^a +, soluble; —, insoluble; +/-, swollen polymers or gel-like solution

good solvents, with two very noticeable exceptions: hexamethylphosphoramide (no. 24) and *N,N,N',N'*-tetramethylmethylphosphonic acid diamide (no. 25). These latter two species also show the highest molar volumes and refractivities; the observed insolubility of the polyzwitterion indicates that more complex structural

features are probably involved in the solubility properties, such as, for instance, increased steric hindrance around the dipolar P=O bond. The aprotic good solvents of the polyzwitterion belong to two main classes, essentially defined by the presence of the dipolar C=O or S=O bonds, as outlined below, either in the acyclic or cyclic

solubilization of the polyelectrolyte P.III, which remains insoluble even in a highly concentrated solution of sodium chloride (6 M) and bromide (7 M) just below saturation. In the same way, for the most polarizable and efficient 'soft' anions, I^- and SCN^- , and for the bulky hard anion ClO_4^- , the CSC values for P.III must be increased by a factor of 10^3 with respect to those related to the poly(sulfopropylbetaine)s to reach solubility. These drastic differences observed between the two polymers suggest dissimilar solvation mechanisms. If specific ion-dipole interactions are likely to occur for the hydrophilic polysulfonate at low ionic strength²⁹, the solvation of the hydrophobic polyelectrolyte becomes efficient at such high ionic strengths that it rather involves non-specific interactions. A variety of ionic complexes may occur in concentrated salt solutions ($ZnCl_4(H_2O)^{2-}$ for $ZnCl_2 > 0.5 \text{ mol l}^{-1}$, for instance³⁰) which have to be considered as new binary solvents quite different from their dilute counterparts.

The analogy between the polyelectrolyte and polyacrylonitrile (PAN) may be stressed again: PAN is soluble in concentrated aqueous solutions of both $NaSCN$ ³¹ and $ZnCl_2$ ³², and the CSC values measured for a sample with $DP_w = 1.9 \times 10^3$ are of the same order of magnitude, especially for $ZnCl_2$, as those related to P.III ($DP_w = 4.8 \times 10^3$).

Viscosimetric chain expansion of the polyelectrolyte as a function of the solvent polarity

With respect to intrinsic viscosity measurements, some zwitterionic copolymers, obtained from 'ion-pair comonomers' and characterized by an alternating distribution of positive and negative charges in the lateral groups, show significant deviations from the Huggins equation³³. In all the solvents tested, either pure (dielectric permittivities within the range 12.4–77.5) or aqueous salt solutions, we did not observe such deviations as found for most other polyelectrolytes. The comparison in TFE solution between the polyelectrolyte P.I of $M_w = 2.8 \times 10^6$ and its homologous cationic polyelectrolyte of $M_w = 11 \times 10^6$ — the counterion has much the same structure as the anionic site of the zwitterion function — deserves special attention. A typical polyelectrolyte behaviour may be clearly detected at low concentration for the polysalt, in spite of the relatively weak dielectric permittivity of the solvent ($\epsilon = 26.7$), and only in that case, as shown in Figure 2. This feature, observed in a moderately dissociating organic medium¹⁴ as well as in water, emphasizes one of the major differences between polyelectrolytes and polyelectrolytes.

The values of the intrinsic viscosities and of the Huggins constants, K'_H , of polymer P.III measured in various solvents are given in Table 2. As a general and expected trend, K'_H is a decreasing function of the chain expansion (measured by $[\eta]$), but no quantitative information may be derived from these variations. K'_H always remains lower than 0.52, the theoretical value calculated for a random coil in a θ solvent³⁴. Moreover, linear variations of C/η_{sp} versus C (Heller equation), measured for a given polymer sample in a series of solvents, are expected to converge to the so-called 'crossover' concentration, allowing us to derive a value of its intrinsic viscosity in a θ solvent, and thus the unperturbed dimensions, K_θ , of the chain³⁵; this approach fails for our measurements (probably performed in too low a concentration range).

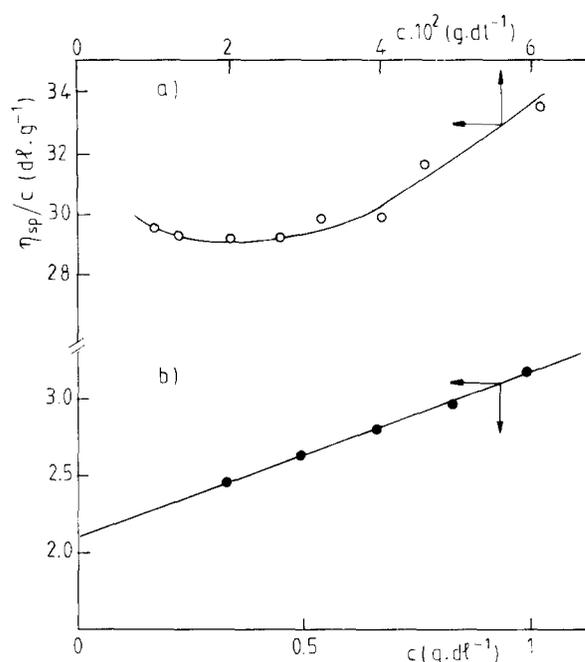


Figure 2 Huggins plot of the viscosity data in TFE solution at 25°C: ○, polyelectrolyte ($M_w = 11 \times 10^6$); ●, polyelectrolyte P.I ($M_w = 2.80 \times 10^6$)

Table 4 Correlation matrix for dipolar aprotic solvents

	MR	μ	$-\Delta H_{BF_3}^0$	$[\eta]$
MR	1	0.5411	0.2240	0.8599
μ		1	-0.2470	0.7768
$-\Delta H_{BF_3}^0$			1	0.1543
$[\eta]$				1

For the solvent set under study, the solubility parameter approach in its one-dimensional (Hildebrand) or more sophisticated three-dimensional³⁶ form does not allow rationalization of the $[\eta]$ variations with solvent nature. Since they directly reflect polymer-solvent interactions, they were tentatively interpreted through linear multiparametric correlation analysis using the same solvent polarity parameters as for the previous determination of the solubility map.

The correlation matrix for dipolar aprotic solvents is given in Table 4. The MR , μ and $-\Delta H_{BF_3}^0$ are independent descriptors and regression analysis leads to:

$$[\eta](\text{dl g}^{-1}) = -6.27 + 0.065 MR(\text{ml g}^{-1}) + 1.42 \mu (\text{D})$$

with regression coefficient $R(8) = 0.946$ and mean square standard deviation, $\sigma = 0.224$ (see Figure 3).

The introduction of the third term, $\Delta H_{BF_3}^0$, is not statistically correct for the restricted number of solvents involved³⁷. Using centred variables, in order to take into account their different variation ranges³⁸, the correlation allows estimation of the respective contributions of dipole-induced dipole and dipole-dipole interactions to the chain expansion: 59 and 41% respectively. Although purely empirical and not accurate enough to be used as a predictive tool, the previous correlation remains of definite interest since it points out that the solvent molar refractivity, MR , and polarity, μ , are of almost the same importance with respect to the chain expansion. A very rough and straightforward quadrupole calculation allows

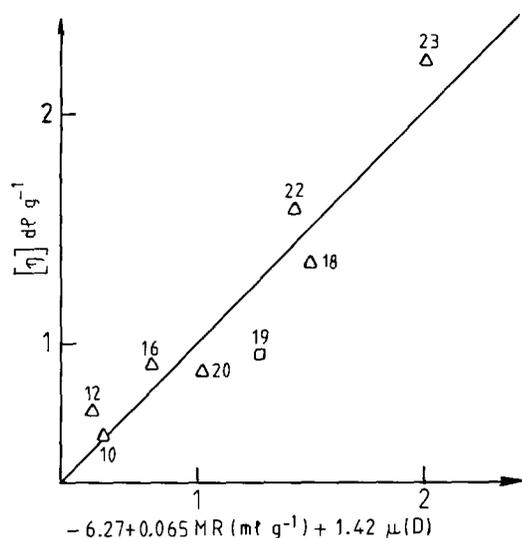


Figure 3 Correlation between the intrinsic viscosity of the polyzwitterion P.III at 25°C in various dipolar aprotic solvents and their polarity parameters, MR and μ ; \square , $|\mu|_{\text{exp}} - |\mu|_{\text{calc.}}| > 1\sigma$ (standard deviation)

estimation of the dipole-dipole interaction between the zwitterion ($\mu = 25.9$ D, distance between the charged sites $d = 5.40$ Å) and a DMF molecule ($\mu = 3.88$ D, $d = 0.85$ Å) placed symmetrically either in a parallel or antiparallel conformation at a distance r in DMF solution ($\epsilon = 36.7$). The energy differences between these two conformations are about 2 and $0.7 kT$ for distances $r = 3$ and 5 Å, respectively, which appear quite reasonable taking into account steric hindrance of the interacting species. Partial orientation of the solvent molecules in the first solvation layer of the zwitterion cannot be ruled out at room temperature.

For protic solvents, the $[\eta]$ variations are an increasing function of the hydrogen-bond-donating power of the solvent, α (see Table 2).

Temperature effects on the polyzwitterion solubility in DMF and in aqueous salt solution

For P.V ($M_w = 0.22 \times 10^6$) solutions in DMF within the concentration range 0.05–20 wt%, phase separation occurs on heating at moderate temperatures ($T_c \approx 75$ – 85°C), as shown in Figure 4. The polymer remains insoluble up to the boiling point (T_E (DMF) = 153°C), and experiments carried out under pressure (beyond the scope of the present work) would be necessary to check the possible occurrence of a homogeneous phase at higher temperatures (closed-loop phase diagram). Moreover, no phase separation occurs on cooling down to the freezing point of the solution (T_M (DMF) = -60.4°C). The system is thus characterized by an *LCST* and the corresponding θ temperature may be roughly estimated according to the semiempirical method of Cornet and Ballegooijen³⁹; the linear variations $T_c^{-1} \propto \log \Phi_p$, where Φ_p is the volume fraction of the polymer in the solution, allow extrapolation to a lower θ temperature according to $T_c \rightarrow \theta$ when $\Phi_p \rightarrow 1$.

Linearization of the experimental data shown in Figure 5 (regression coefficient of 0.960 over 10 data points) leads to $\theta = 65.8 \pm 1^\circ\text{C}$. This typical *LCST* is not restricted to DMF solutions, but may also be identified in some other dipolar aprotic solvents. For 1 wt% polymer P.II ($M_w = 2.14 \times 10^6$) solutions compare, for

instance, the cloud point temperatures of 62°C in *N,N'*-dimethylethyleneurea (no. 18), of 64°C in DMF (no. 12) and of 75°C in *N*-methylpyrrolidone (no. 19), while no phase separation occurs in dimethylsulfoxide (no. 16), *N*-methyloxazolidinone (no. 20) or *N,N'*-dimethylpropyleneurea (no. 23) below 150°C where irreversible discoloration of the solution starts to develop. Some preliminary experiments show analogous *LCST* behaviour for the parallel acrylate series and, more interestingly, for the closely related poly(ammonio-propoxydicyanoethenolate)s, which carry homologous zwitterionic side groups of slightly higher dipole moment ($\mu = 30.8$ D). In the latter case, the cloud point temperatures appear systematically lower, whatever the solvent. The occurrence of an *LCST* in a rather low temperature range is not uncommon for polar polymers in aqueous solution⁴⁰, but more scarce in organic solvents^{41–43}. It does not arise from simple free-volume effects as for non-polar systems, where demixing most often occurs in the vicinity of the critical liquid-vapour point of the solvent, but more probably from the loosening of polymer-solvent specific interactions when increasing temperature; see the term 'quasi-*LCST*' recently coined by Cowie and Swinyard⁴³ for such phase separation in polar systems.

The phase diagrams of the ternary systems water-polyzwitterion-salt are characterized by a *UCST*; solubilization occurs upon heating over a critical temperature

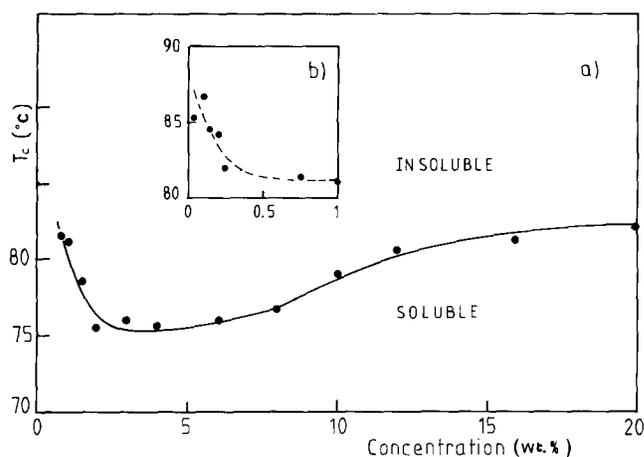


Figure 4 Phase diagram of polyzwitterion P.V in DMF. The insert (b) shows the lower concentration range of (a) at an expanded scale

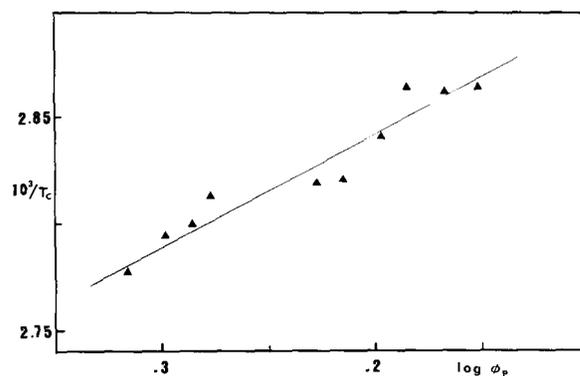


Figure 5 Variations of the cloud point temperature T_c (*LCST*) with the polymer volume fraction Φ_p for polyzwitterion P.III in DMF solution

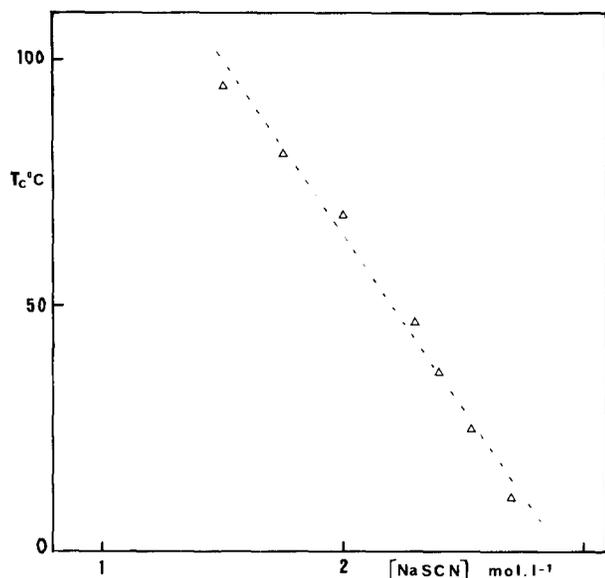


Figure 6 Variations of the cloud point temperature T_c (UCST) with the salt concentration for 1 wt% solution of polyzwitterion P.II in NaSCN aqueous solution

T_c for a given salt concentration, as already observed in the case of poly(ammonium sulfopropylbetaine)s^{8,24}. For polymer P.II ($M_w = 2.14 \times 10^6$) in aqueous NaSCN solution, the cloud point temperatures, T_c , are a linear, strongly decreasing function of temperature, $dT_c/d[\text{NaSCN}] = -70^\circ\text{C l mol}^{-1}$, as shown in Figure 6 (regression coefficient of -0.993 over seven data points).

Salt effects on the expansion of the polyzwitterion coil in aqueous and organic solvents

The influence of added salts on the expansion of the polyzwitterion coil in dilute solution at 25°C was studied through intrinsic viscosity measurements restricted to a single polymer sample. The experimental results are given in Figures 7–9 for water (polymer P.III), DMF and TFE (polymer P.IV) as solvents.

In water, the chain expansion is an increasing function of the salt concentration with a levelling effect for the highest concentrations (Figure 7); the more polarizable SCN^- anion is the more efficient. Pure ethylammonium nitrate (EAN), a liquid salt of outstanding polarity in terms of ion–dipole and hydrogen bonding interactions⁴⁴, affords a quantitatively ionized solvent; it shows only moderate solvation power towards the zwitterionic chain, fairly similar to that of 3-methyl-2-oxazolidinone (no. 20) ($[\eta] = 0.81$ and 0.88 dl g^{-1} in EAN and solvent no. 20, respectively). EAN is also a moderately good solvent for poly(ammonium sulfopropylbetaine)s⁴⁵, but the behaviours of the two polyzwitterions in its aqueous solutions are very different: compare the increase in $[\eta]$ by a factor of about 2.5 when EAN concentration increases from 6 to 11 mol l^{-1} (pure salt) for the cyano hydrophobic chain, with the remarkable invariance of $[\eta]$ ($[\eta] = 2.2 \text{ dl g}^{-1}$ for $M_w = 5.7 \times 10^6$) over the very broad salt concentration range of 0.75 – 11 mol l^{-1} for the hydrophilic sulfonate chain⁴⁵.

Comparison of the influence of the anion structure for lithium salts in DMF and for homologous tetramethylammonium salts in TFE (lithium species are not sufficiently soluble) indicates major differences between the highly dipolar aprotic and the moderately polar but

highly protic solvents. Two main features may be emphasized.

1. In DMF solution, all the lithium salts promote a rather strong chain expansion, with a levelling effect for concentrations higher than about 0.1 M , and the order of increasing efficiency, $\text{ClO}_4^- < \text{I}^- < \text{Br}^- < \text{Cl}^-$, is the

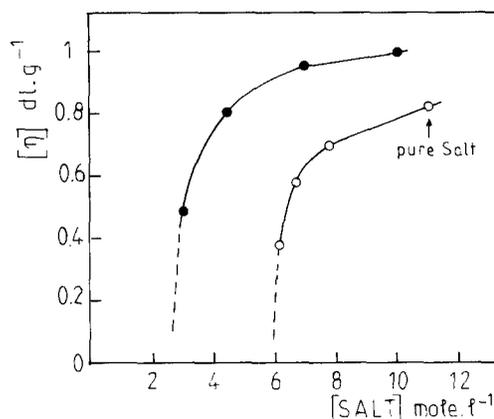


Figure 7 Variations of the intrinsic viscosity of polyzwitterion P.III in aqueous solution at 25°C with salt concentration: ●, KSCN; ○, $\text{C}_2\text{H}_5\text{NH}_3^+$, NO_3^-

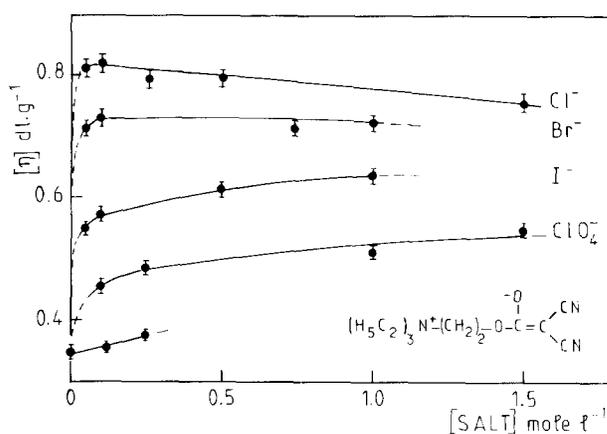


Figure 8 Variations of the intrinsic viscosity of polyzwitterion P.IV in DMF solution at 25°C in the presence of lithium salts and of a model zwitterion

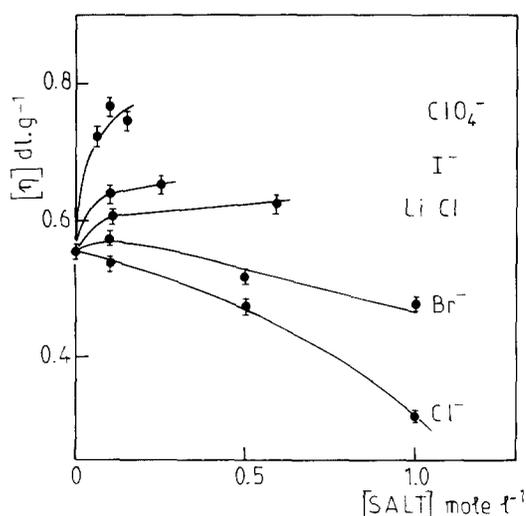
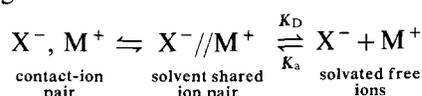


Figure 9 Variations of the intrinsic viscosity of polyzwitterion P.IV in TFE solution at 25°C with tetramethylammonium salt concentration

opposite to that observed in aqueous solution for poly(ammonium sulfoalkylbetaine)s⁵⁻¹⁰.

- In TFE solution, tetramethylammonium salts promote a moderate chain expansion only in the case of the highly polarizable soft anion or bulky hard anion, with an increasing order of efficiency $I^- < ClO_4^-$, identical to that observed in water solution for poly(ammonium sulfoalkylbetaine)s⁵⁻¹⁰. Hard anions, however, induce a progressive chain collapse, Cl^- being the more efficient.

In all cases, addition of salts enhances the kinematic viscosity of the pure solvents, and the role of the ionic species cannot be identified with any effect of structure breaking of the weakly self-associated DMF or TFE. The observed salt effects result from the perturbation of dipolar or electrostatic intramolecular interactions within the polymer coil in an electrolyte solution, or from direct specific interactions of the zwitterionic chain with the wide variety of ionic species present in the medium. The structure and relative amounts of the latter species depend essentially on the solvation and dissociation equilibria, according to:



With respect to this general scheme, the various salts in DMF and TFE afford a broad variety of situations. The dissociation equilibrium is monitored mainly by the dielectric permittivity of the solvent, DMF ($\epsilon = 36.7$) being a more dissociating medium than TFE ($\epsilon = 26.7$), but the nature and the concentration of the salt are also important parameters. A knowledge of the dissociation constants, K_D , allows calculation of the amount of free ions for sufficiently dilute solution, and then derivation, in the usual way¹¹, of the values of the Debye-Hückel reciprocal length, χ^{-1} , related to a distance over which electrostatic interactions are strongly reduced; some representative values are given in Table 5 for a constant salt concentration of 0.1 mol l^{-1} . It is clear that all the observed effects cannot be rationalized by taking into account only the screening of electrostatic interactions, as estimated in a first approach according to the Debye-Hückel theory transposed to weakly dissociating organic solvents. Compare more especially the behaviour of ClO_4^- and Cl^- anions in TFE solution, which lead to opposite effects on the coil expansion in spite of similar χ^{-1} values.

More specific ion-dipole interactions between the electrolyte and the zwitterionic units are probably involved in the chain solvation. With respect to anion solvation, DMF and TFE show opposite trends. In DMF, an aprotic and rather strongly basic solvent (see the $\Delta H_{BF_3}^0$ scale, for instance), the cations are strongly solvated and the anions are nearly 'naked' species

(compare the solvated radii of ClO_4^- and Li^+ of 3.3 and 5.1 Å, respectively)⁴⁶. TFE, however, shows rather low nucleophilicity and one of the highest hydrogen-bond-donating powers (see the previous α scale), resulting in weak and in very strong solvation of the cations and anions, respectively. For anions, for instance, these features may be estimated in a more quantitative way by calculating the standard molar Gibbs free energies of their transfer from DMF to TFE, $\Delta G^0(\text{DMF} \rightarrow \text{TFE})$, from the literature data⁴⁷ $\Delta G^0(\text{H}_2\text{O} \rightarrow \text{DMF}$ or TFE) according to:

$$\Delta G^0(\text{DMF} \rightarrow \text{TFE}) = \Delta G^0(\text{H}_2\text{O} \rightarrow \text{TFE}) - \Delta G^0(\text{H}_2\text{O} \rightarrow \text{DMF})$$

The highly negative values of $\Delta G^0(\text{DMF} \rightarrow \text{TFE})$ and their decrease with decreasing anion size (-58.3 and $-28.4 \text{ kJ mol}^{-1}$ for Cl^- and I^- , respectively, for instance) stress the outstanding influence of hydrogen bonding in the anion solvation.

Turning back to the salt effects, and more specifically to the influence of the anion structure on the polyzwitterion coil expansion, only some tentative correlations may be drawn, as follows.

- In DMF solution, the order of increasing efficiency of the naked anions is parallel to that of their charge density (decreasing size and polarizability): possible enhancement of the anion-dipole interaction.
- In TFE solution, strong anion solvation result in a reverse order parallel to that of their hydrogen-bond-accepting power according to Marcus⁴⁸ ($ClO_4^- < I^- < Cl^-$). However, no clear explanation can be advanced for the shift from a coil expansion to a coil collapse when increasing the anion solvation. Comparison of $LiCl$ and Me_4NCl , which have opposite effects, again shows that the polyzwitterion-ion interactions involve more complex mechanisms.
- Finally, for high salt concentrations ($> 0.1 \text{ M}$), complex multiple ion aggregates are likely to occur in these solvents, possibly leading to the levelling effects such as those observed in DMF.

Since coil expansion in organic salt solution appears to involve strong specific ion-dipole interactions at the lateral zwitterionic groups of the polymer chain, we try to model the ternary system DMF-polyzwitterion-ion using the well known solvatochromy of the Dimroth-Reichardt dye, which is a zwitterion of the pyridinium phenolate type²³ ($\mu = 14.7 \text{ D}$). Its long wavelength absorption band is related to the formation of an intramolecular charge transfer (ICT) complex, and shows an outstanding sensitivity to the polarity of its microenvironment (the dipole moment decreases by about 8.7 D when going from the ground to the excited state), and thus to the presence of salts in organic solvents⁴⁹. The variations of the wavelength and of the molar absorptivity of the dye with lithium salt concentration were measured in DMF solution, as shown in Figure 10. Increasing salt concentration results in a strong hypsochromic shift for dilute solutions ($[\text{salt}] \leq 0.05 \text{ mol l}^{-1}$), perchlorate anion being slightly more efficient than the chloride one: for 0.05 M solution, the increases in transition energy, E_T , are 23 and 27 kJ mol^{-1} for Cl^- and ClO_4^- respectively, with respect to that in pure DMF. For higher concentrations, salt effects level off. These characteristic features emphasize

Table 5 Dissociation constants and Debye-Hückel lengths of 0.1 M solutions of various salts in DMF and TFE at 25°C

	DMF ⁵²		TFE ¹⁴		
	LiCl	LiClO ₄	LiCl	(Me) ₄ NCl	(Me) ₄ NClO ₄
$K_D \times 10^2$	2.70	∞	0.52	3.45	2.17
χ^{-1} (Å)	10.4	6.6	12.4	8.4	9.2

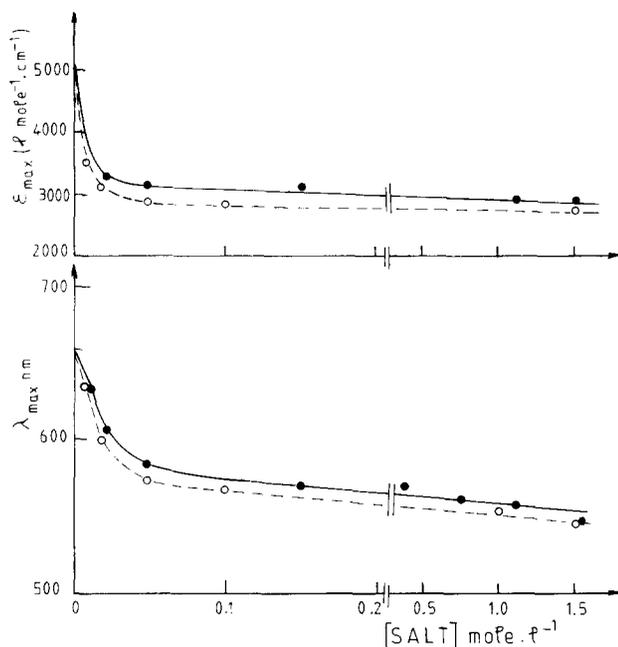


Figure 10 Influence of the salt concentration on the wavelength λ_{\max} and molar absorptivity ϵ_{\max} of the ICT transition of the Dimroth-Reichardt betaine dye observed in DMF solution: ●, LiCl; ○, LiClO₄

that the presence of added salts promotes a very strong stabilization of the zwitterionic ground state of the dye; it probably promotes, in a parallel way, the solvation of the zwitterionic chain observed in the macromolecular system. However, the order of anion efficiency is reversed.

Finally, chain expansion in DMF solution may also be promoted by strongly dipolar species such as the low molecular weight model zwitterion, triethylammonio ethoxydicynoethenolate, but with a drastically lower efficiency than for electrolytes at the same concentration: see Figure 10. This behaviour is identical to that observed in the homologous aqueous solutions of poly(ammonium sulfopropylbetaine)s^{4,5}.

CONCLUSIONS

The study of the solubility properties of poly[2,2-dicyano-1-[2-(2-(methacryloyloxy)ethyl)dimethylammonio]-ethoxy]-ethenolate], chosen as a representative polymer of the whole class of poly(ammonio alkoxydicynoethenolate)s, has shown a general behaviour reminiscent of that of the classical hydrophilic poly(ammonium sulfopropylbetaine)s, but with very specific differences resulting from the hydrophobicity and high polarizability of the anionic site of their zwitterionic side groups. Weakly self-associated and highly protic alcohols, such as fluorinated alcohols, are common solvents, and this feature emphasizes that strong hydrogen bonding to the anionic site of the zwitterion is a very efficient solvation process for the chain. However, the solubility of the hydrophobic polyzwitterion in dipolar aprotic solvents is in sharp contrast with the insolubility of the poly(sulfopropylbetaine)s. The LCST behaviour and the salt effects observed in DMF solution are of special interest; they may be considered within the more general field of the thermodynamics of highly polar polymer-organic solvent systems, where new experimental data are always needed. The system under investigation may be used as a model

for more thorough analysis with respect to both aspects: LCST within the framework of recent theoretical approaches⁵⁰, and salt effects in connection with electrochemistry and ion-dipole effects in these solutions of weak electrolytes.

The morphological and hydrodynamic properties of the polyzwitterion in dilute solution will be analysed in a forthcoming paper within the classical framework of the two-parameter theories: determination of the unperturbed dimensions, chain rigidity and of the Flory χ interaction parameter in DMF (temperature and salt effects), TFE and 3 M NaSCN aqueous solution.

ACKNOWLEDGEMENT

The authors are indebted to Mrs H. Bellissent for her efficient technical assistance throughout this work.

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