

# Poly(sulfopropylbetaines): 6. Catalysis of inter-ionic reactions in aqueous solution by polyzwitterions

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The 'catalytic' effects of polyzwitterions on aqueous inter-ionic reactions were studied through the analysis of the influence of a representative zwitterionic macromolecule, poly[diethyl-(2-methacryloyloxyethoxy-2-ethyl)-1-(3-sulfopropyl) ammonium betaine], on two model inter-anionic and inter-cationic reactions, i.e. oxidation of ferrocyanide by persulfate and aquation of a bromopentaamminecobalt complex. The anionic system is clearly accelerated, but considerably less than with a cationic polyelectrolyte of similar structure, poly[triethyl-(2-methacryloyloxyethoxy-2-ethyl)-ammonium methylsulfonate]. A small model zwitterion,  $(C_2H_5)_3-N^+-(CH_2)_3-SO_3^-$ , has no effect. The inter-cationic reaction is not accelerated by the polyzwitterion. Copyright © 1996 Elsevier Science Ltd.

**(Keywords: polyzwitterions; catalysis of inter-ionic reactions; oxidation of ferrocyanide by persulfate)**

## INTRODUCTION

Water-soluble polyzwitterions (PZs) of the vinyl or methacrylic type with zwitterionic ammonioalkylsulfonate groups<sup>1–6</sup> have been shown to interact with ionic species in an original way compared to polyelectrolytes (PEs)<sup>5–12</sup>. In the presence of dissolved salts, they display the so-called 'antipolyelectrolyte' behaviour, i.e. their chains expand with increasing ionic strength, resulting in a better water solubility and higher intrinsic viscosity values. The direct short-range interaction of PZs with positively or negatively charged ions is well ascertained through the analysis of the corresponding aqueous systems at a very local level: (a) change of the microenvironment of the sulfonate anionic site of polysulfobetaines in the presence of NaCl is revealed by laser Raman spectroscopy<sup>6</sup>; (b) solvatochromy of methyl orange absorption, enhancement of the 8-anilino-naphthalene-1-sulfonate fluorescence and rate enhancement of the 6-nitrobenzoisoxazole-3-carboxylate unimolecular decomposition are observed in the presence of the PZ, as a result of the binding of these three anionic probes to the polymer chain<sup>13</sup>. Moreover, association of PZs with PEs of both signs, leading to weak 'interpolymer complexes'<sup>14</sup>, has also been recognized. On the other hand, PEs are also known to accelerate reactions between separated small ions of the same sign but opposite to the charges on the polymer. This 'catalytic' effect<sup>15,16</sup>, sometimes considered as a very simplified model of the enzymic catalysis<sup>16</sup>, has been shown to proceed through an increased concentration of both reacting ions in the surroundings of the polymer chain, raising their collision probability and resulting in a clearly higher value of the rate constant  $k$ . It may thus be

of interest to see how a PZ acts as a potential catalyst in reactions between ionic species of a given sign: may it be considered more or less as a polyampholyte with a balance between electrostatic attracting and repelling properties or has it a specific behaviour typical of the polyzwitterionic structure?

These properties may obviously vary from one PZ to another, but before undertaking an exhaustive investigation, it seemed necessary, in a first step, to look for the catalytic behaviour of a PZ previously studied in our laboratory<sup>4,10,13,14</sup>. Poly[diethyl-(2-methacryloyloxyethoxy-2-ethyl)-1-(3-sulfopropyl) ammonium betaine] has the major advantage of being fairly soluble in water at room temperature. The results were compared to those obtained with a model PE showing identical structure of the charged sites, poly[triethyl-(2-methacryloyloxyethoxy-2-ethyl) ammonium methylsulfonate], and with a low molecular weight model zwitterion (Z), triethylammonium sulfopropylbetaine. As test reactions, we chose two well known interionic reactions which are able to be catalysed by PEs: the oxidation of ferrocyanide by a persulfate salt for the anionic reaction<sup>17–20</sup> and the aquation of a bromopentaamminecobalt complex in the presence of a mercuric salt for the cationic reaction<sup>21–27</sup>.

In all the following text, PZ, PE and Z represent the polyzwitterion, the model polyelectrolyte and the model zwitterion, respectively.

## EXPERIMENTAL

### Materials

*Salts.* Potassium ferrocyanide ( $K_4Fe(CN)_6 \cdot 3H_2O$ ) [R.P. Normapur pour analyses (99%), Prolabo] was

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used without further purification. Although quite stable in the solid state, it is slowly oxidized to the corresponding ferricyanide in aqueous solution, with reaction extents  $\alpha$  depending on the experimental conditions as typified by the following data: for a  $1.00 \times 10^{-4}$  M solution after 48 h,  $\alpha = 0.30$  at room temperature, 0.20 at  $5^\circ\text{C}$  and 0.04 at  $5^\circ\text{C}$  in the presence of ethylenediaminetetraacetic acid (EDTA,  $10^{-5}$  M, see further). Only freshly prepared solutions were thus systematically used for kinetic experiments.

Potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ) [ACS reagent (>99%), Aldrich] was stored at  $-15^\circ\text{C}$  without further purification. Its aqueous solutions (EDTA/ $\text{H}_2\text{O}$ ,  $10^{-5}$  M) are quite stable and they never show any trace of decomposition (sulfate formation identified by addition of  $\text{BaCl}_2$ ), when kept up to eight days, even at room temperature.

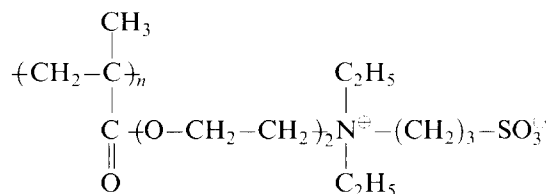
Mercury (II) nitrate [ $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ ] [Rectapur (98%), Prolabo] was dehydrated *in vacuo* ( $10^{-2}$  torr) at  $50^\circ\text{C}$ , just before use.

Bromopentaamminecobaltic nitrate [ $[\text{Co}(\text{NH}_3)_5\text{Br}(\text{NO}_3)_2]$ ] was prepared from  $\text{CoCO}_3 \cdot (\text{H}_2\text{O})_x$  (Aldrich) by simplifying the literature procedure<sup>25</sup>. The intermediate bromopentaammine cobaltic bromide was poured as a powder into an excess of concentrated nitric acid (65 wt %) at room temperature, without previous dissolution in sulfuric acid as indicated in the original method. After one night the emission of red vapour ceased and the remaining violet powder was filtered and recrystallized from hot water.

Analysis:	$\text{H}_{15}\text{N}_7\text{O}_6\text{BrCo}$ ( $M = 348.04$ ).
Calculated (%):	H 4.34 N 28.17 O 27.59
	Br 22.96 Co 16.93.
Found (%):	H 4.2 N 27.4 O 28.0 Br 22.7
	Co 17.7.

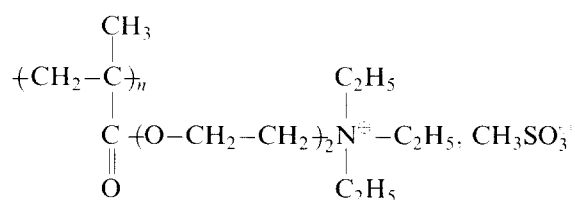
The complex cannot be stored for a long time in aqueous solution. Even in the presence of stabilizing  $\text{HNO}_3$  ( $10^{-3}$  M), concentrated violet stock solutions ( $10^{-3}$  M) readily turn brown after some hours. After seven days the initial and typical 254 nm absorption decreases by a factor of 10. Only fresh solutions were thus used for the kinetic measurements.

*Zwitterions and polyelectrolyte.* PZ: poly[diethyl-(2-methacryloyloxyethoxy-2-ethyl)-ammonio propane-3-sulfonate]:



was prepared by free radical polymerization in aqueous solution of the corresponding monomer as described before<sup>4</sup>. In order to avoid the formation of aggregates, which strongly disturb or even inhibit interionic reactions in solution, it was necessary to use PZ samples recovered by freeze-drying of an aqueous precursor solution instead of the initial sample directly recovered by precipitation into methanol at the end of its synthesis. The average molecular weight measured by light-scattering was  $M_w = 4.35 \times 10^6$  [ $(dn/dc) = 0.144 \text{ ml g}^{-1}$  in aqueous 0.1 M NaCl at a wavelength of 632 nm].

PE: poly[triethyl-(2-methacryloyloxyethoxy-2-ethyl)-ammonium methylsulfonate]:



The corresponding monomer was prepared by quaternization of diethylaminoethoxyethyl methacrylate<sup>4</sup>. To 11.5 g ( $5 \times 10^{-2}$  mol) of the latter were added 6.5 g ( $5 \times 10^{-2}$  mol) of ethyl methanesulfonate in 100 ml of acetonitrile as solvent, in the presence of 20 mg of *m*-dinitrobenzene as a polymerization inhibitor. The mixture was heated at  $60^\circ\text{C}$  for 48 h and then poured into an excess of diethyl ether. The monomer, separated as an oil, was vacuum-dried. Yield = 40%.

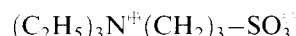
<sup>1</sup>H n.m.r. ( $\text{CDCl}_3$ )  $\delta$ : 6.1 and 5.6 (2s, 2H,  $\text{CH}_2=$ ); 4.3 (*t*, 2H,  $\text{COOCH}_2$ ), 3.8 (*m*, 4H,  $\text{CH}_2\text{-O-CH}_2$ ), 3.5 [*m*, 6H,  $\text{N}^+(\text{CH}_2)_3$ ], 2.8 (*s*, 3H,  $\text{CH}_3\text{-SO}_3$ ), 1.9 (*s*, 3H,  $\text{CH}_3\text{-C=}$ ), 1.4 (*t*, 6H,  $\text{N}(\text{CH}_2\text{-CH}_3)_2$ ).

The free radical polymerization of the monomer was carried out at  $60^\circ\text{C}$  in homogeneous aqueous solution, under argon, during 16 h: [monomer] = 0.6 M, [initiator] (4,4'-azobis-4-cyanovaleric acid) =  $0.6 \times 10^{-2}$  M. The polymer was separated from the monomer by dialysis and finally recovered by freeze-drying. Yield: 85%.

Analysis:	$\text{C}_{15}\text{H}_{31}\text{O}_6\text{NS.H}_2\text{O}$ ( $M = 371.50$ ).
Calculated (%):	C 48.50 H 8.95 O 30.15 N 3.77
	S 8.63.
Found (%):	C 49.1 H 9.0 O 30.5 N 3.6
	S 8.1.

The weight average molecular weight was determined by light scattering:  $M_w = 8.17 \times 10^6$  [ $(dn/dc) = 0.121 \text{ ml g}^{-1}$  in aqueous 0.1 M NaCl at a wavelength of 632 nm].

Z: 3-triethylammonio-1-propanesulfonate (SB):



was prepared as previously described<sup>28</sup>.

#### Viscometry measurements

Specific viscosity ( $\eta_{sp}$ ) measurements were performed on an automatic Ubbelohde type dilution viscometer at  $25^\circ\text{C}$ , using a maximum concentration of  $10^{-2}$  M for the PZ ( $0.35 \text{ g dl}^{-1}$ ).

#### Kinetic measurements by spectrophotometry

For the kinetic measurements, water was triply distilled in a quartz vessel. In the case of the anion-anion reaction, EDTA [ACS reagent (99.5%), Aldrich] was added to the solvent ( $1 \times 10^{-5}$  M) in order to prevent any catalytic effect from traces of heavy metal ions<sup>19</sup>. A  $10^{-3}$  M solution of nitric acid was used as solvent for the cation-cation reaction in order to repress hydrolysis of the complex cobaltic salt<sup>25</sup>.

The kinetics of the catalysed interionic reactions were monitored through the variations of the optical absorption of one of the appearing or disappearing species, measured on a UV-2101-PC Shimadzu spectrophotometer, working in the timing mode. The reacting

solutions were studied in special double-wall cells ( $\pm 0.1^\circ\text{C}$ ), thermostatted by water circulation.

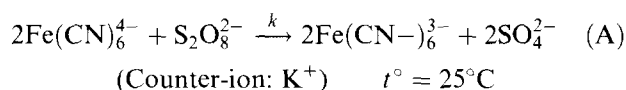
**System  $\text{K}_4\text{Fe}(\text{CN})_6 + \text{K}_2\text{S}_2\text{O}_8/\text{PZ}$ , Z or PE.** The freeze-dried PZ was dissolved in the aqueous EDTA solution ( $10^{-5}\text{M}$ ) at room temperature and kept overnight under stirring. Just before reaction, the calculated amount of crystalline  $\text{K}_4\text{Fe}(\text{CN})_6$  was introduced into this solution, which was then quickly mixed with a calculated amount of a  $\text{K}_2\text{S}_2\text{O}_8$  stock solution in order to reach a stoichiometric ratio  $[\text{K}_2\text{S}_2\text{O}_8]/[\text{K}_4\text{Fe}(\text{CN})_6] = 30$ . The reaction mixture was immediately transferred into the spectrophotometer cell preheated at  $25^\circ\text{C}$ . The delay between the mixing and the start of the optical density recording never exceeded 30 s.

The same procedure was used in the cases of the model zwitterion Z and the model polyelectrolyte PE, where dissolution in the aqueous EDTA does not require an overnight stirring at room temperature. In the latter case, when  $[\text{PE}] > 10^{-5}\text{M}$ , polymer precipitation partially occurs as soon as a salt is added and the spectroscopic measurements are performed in the supernatant liquid phase.

**System  $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{NO}_3)_2 + \text{Hg}(\text{NO}_3)_2/\text{PZ}$ .** The freeze-dried PZ readily dissolved in a freshly prepared solution of the cobaltopentaammine in  $10^{-3}\text{M}$   $\text{HNO}_3$ . At the same time a  $\text{Hg}(\text{NO}_3)_2$  solution was prepared in the same solvent by gentle heating. Both solutions were placed in a thermostat at  $15^\circ\text{C}$ , then mixed and immediately transferred to the spectroscopic cell maintained at the same temperature. The delay between mixing and measuring lies between 20–30 s.

## KINETIC RESULTS

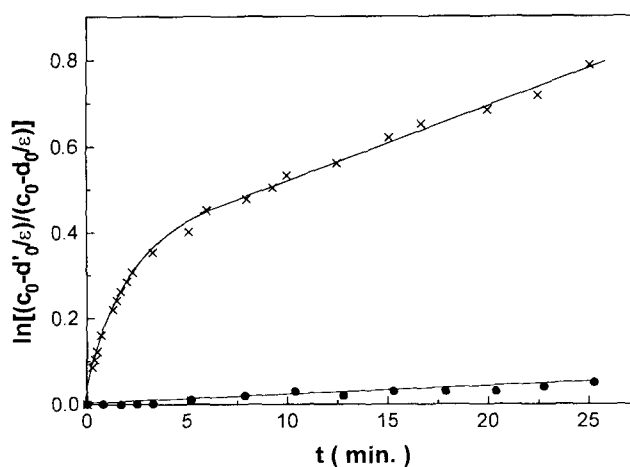
### Anion–anion reaction



The concentrations of the reacting salts and of the PZ were selected in order to meet several requirements, as detailed below.

- $[\text{K}_2\text{S}_2\text{O}_8]/[\text{K}_4\text{Fe}(\text{CN})_6] = 30$ : reaction (A) may be thus safely considered as a pseudo-first order process with respect to potassium ferrocyanide.
- $[\text{K}_4\text{Fe}(\text{CN})_6] = 1 \times 10^{-4}\text{M}$ . This optimized concentration represents the best compromise. Higher concentrations would result in initial reaction rates too high to be accurately determined and in solubility problems for the oxidizing reagent (solubility limit of  $\text{K}_2\text{S}_2\text{O}_8 \sim 0.18\text{M}$  at  $25^\circ\text{C}$ ). Lower concentrations would lead to unreliable spectrophotometric values at the limits of detection.
- $[\text{PZ}] \leq 1 \times 10^{-2}\text{M}$  ( $0.35\text{g dl}^{-1}$ ). Beyond this limit, imperfect solubility results in partly aggregated solution where even a very slight turbidity may perturb the spectrophotometric measurements. On the other hand, at concentrations lower than  $10^{-4}\text{M}$  no effect of PZ on the reaction can be detected.

The reaction kinetics were followed through u.v. spectroscopy by monitoring the progressive emergence



**Figure 1** Pseudo-first order kinetics of the anion–anion reaction (A).  $[\text{Fe}(\text{CN})_6^{4-}] = 1 \times 10^{-4}\text{M}$ ;  $[\text{S}_2\text{O}_8^{2-}] = 3 \times 10^{-3}\text{M}$ ;  $[\text{PZ}] = 0$  (●);  $7 \times 10^{-3}\text{M}$  (×)

**Table 1** Pseudo-first order rate constants of the anion–anion reaction (A) in the presence of the polyelectrolyte at various concentrations:  $[\text{Fe}(\text{CN})_6^{4-}] = 1 \times 10^{-4}\text{M}$ ;  $[\text{S}_2\text{O}_8^{2-}] = 3 \times 10^{-3}\text{M}$ .  $\tau_0$  = initial degree of conversion

[PZ] ( $\times 10^3$ ) (M)	$\tau_0$ (%)	$k_1$ ( $\times 10^3$ ) ( $\text{min}^{-1}$ )	$k_2$ ( $\times 10^3$ ) ( $\text{min}^{-1}$ )	W	$k_i$ ( $\times 10^3$ ) ( $\text{min}^{-1}$ )	$k_f$ ( $\times 10^3$ ) ( $\text{min}^{-1}$ )
0.0	0.0	1.4	1.4	—	1.4	1.4
0.1	9.8	0.7	0.7	—	0.7	0.7
1.0	9.8	6.4	1.8	0.12	12.0	1.8
2.0	7.8	30.0	3.1	0.80	48.0	4.6
4.0	26.3	190	5.1	0.80	200	6.0
7.0	41.0	230	19.0	1.00	300	21.0
10.0	44.9	>210	27.0	1.00	>200	27.0

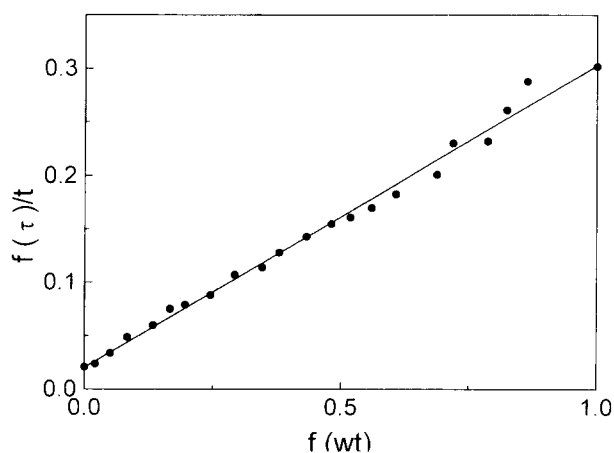
of the ferricyanide ion ( $\epsilon = 1.03 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$  at  $\lambda = 420 \text{ nm}$ )<sup>18</sup>. At the higher concentrations of PZ ( $> 2 \times 10^{-3}\text{M}$ ), the initial reaction rate was so high that oxidation reached a significant initial degree of conversion  $\tau_0$  (Figure 1) between the actual mixing of the two reactants and the first spectroscopic measurement taken as the time origin. The pseudo-first order kinetic equation was thus modified into

$$f(\tau) = \ln[(1 - d_0/\epsilon C_0)/(1 - d/\epsilon C_0)] = kt \quad (1)$$

where  $d_0$  and  $d$  are the solution absorbances at time 0 and  $t$ , respectively (corresponding to degrees of conversion  $\tau_0$  and  $\tau$ ),  $C_0$  is the initial concentration of ferrocyanide, and  $k$  is the pseudo-first order rate constant.

The measurements essentially distinguish two different concentration ranges of added PZ, as shown in Table 1 and illustrated in Figures 1 and 3:

- $[\text{PZ}] < 10^{-3}\text{M}$ : all the experimental data obey equation (1) over very broad conversion ranges ( $\tau = 0$  to  $\sim 95\%$ ) and the PZ has no detectable effect on the oxidation rate. The apparent second-order rate constant  $k/[\text{S}_2\text{O}_8^{2-}]_0 = 0.47 \text{ l mol}^{-1} \text{ min}^{-1}$  is in fairly good agreement with literature data:  $0.56 \text{ l mol}^{-1} \text{ min}^{-1}$ <sup>18</sup>;  $0.55 \text{ l mol}^{-1} \text{ min}^{-1}$ <sup>19</sup>.
- $[\text{PZ}] > 10^{-3}\text{M}$ : the reaction is actually accelerated with respect to the blank experiment ( $[\text{PZ}] = 0$ ). However, the experimental data cannot be accounted



**Figure 2** Fuoss plot of the kinetics of the anion-anion reaction (A), according to equation (2).  $[\text{Fe}(\text{CN})_6^{4-}] = 1 \times 10^{-4} \text{ M}$ ;  $[\text{S}_2\text{O}_8^{2-}] = 3 \times 10^{-3} \text{ M}$ ;  $[\text{PZ}] = 7 \times 10^{-3} \text{ M}$ .  $f(\tau)/t = (1/t)$ .  $\ln[(C_0 - d_0^i/\epsilon)/(C_0 - d_0^i/\epsilon)] = kt$  versus  $f(wt) = 1(1 - e^{-wt})/wt$

for by a single equation (1) and they suggest autoretarded kinetics characterized by two consecutive regimes. The initial and higher rate constant  $k_1$  may be only roughly estimated from the slope at the origin of the quasi-linear plot of  $f(\tau)$  versus  $t$  for low  $t$  values, while the final and lower rate constant  $k_2$  may be well derived from the linear part of the same plot for higher  $t$  values (Figure 1). For the intermediate times, both rate constants  $k_1$  and  $k_2$  contribute with various weights to the overall rate constant.

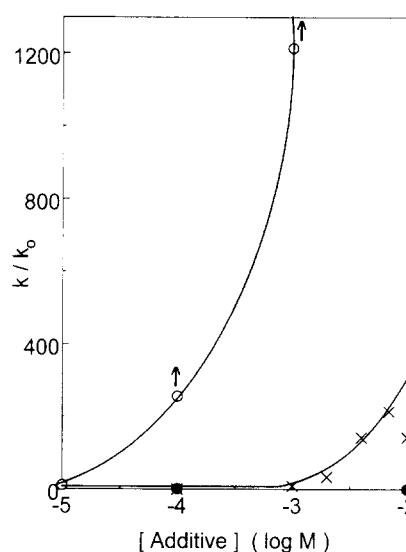
More accurate values of the initial and final rate constants,  $k_i$  and  $k_f$ , were calculated using equation (2), originally proposed by Fuoss *et al.*<sup>29</sup> for the analysis of the autoretarded kinetics observed in the quaternization of poly(4-vinylpyridine) (neighbouring group effects):

$$k = f(\tau)/t = k_f + (k_i - k_f)[(1 - e^{-wt})/wt] \quad (2)$$

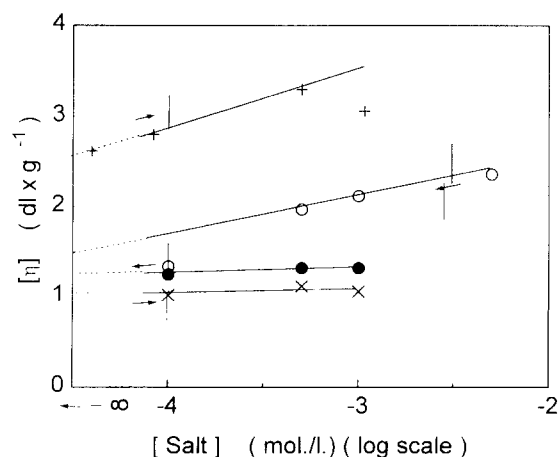
where  $w$  is a semi-empirical adjustable parameter allowing linearization of the  $f(\tau)/t$  variation versus  $(1 - e^{-wt})/wt$ . The abscissa values of 1 ( $t = 0$ ) and 0 ( $t = \infty$ ) correspond to ordinate values of  $k_i$  and  $k_f$ , respectively.

All the experimental data obey equation (2) and this linearization procedure is given in Figure 2 for a representative system (correlation coefficient of 0.996 for 41 data points). Calculated  $k_1, k_2, k_i$  and  $k_f$  values are given in Table 1: as expected  $k_1$  is underestimated with respect to  $k_i$ , especially for  $[\text{PZ}] \geq 10^{-3} \text{ M}$ , while  $k_2$  and  $k_f$  are in good agreement.

Since ion-PZ interactions influence the chain conformation in solution (see in the Introduction the well-known 'antipolyelectrolyte' effect), some measurements of the intrinsic viscosity  $[\eta]$  of PZ solutions were thus performed to test separately the influence of each of the four salts, present in the reacting system, on the chain expansion. The results given in Figure 4 show that only the persulfate anion (always in excess during the catalysed reaction) and the ferricyanide anion lead to a very significant chain expansion ( $[\eta] = 1.00 \text{ dl g}^{-1}$  in pure water). The slopes of the linear variations  $[\eta] = f(\log [\text{salt}])$  may be assumed to reflect more or less the binding constant of the ionic species to the PZ. The strong effects observed more especially for ferricyanide in a very low



**Figure 3** Relative rate constants  $k/k_0$  of the anion-anion reaction (A) in the presence of various ionic or zwitterionic species at different concentrations: (●) small molecule (Z); (○) polyelectrolyte (PE); (×) polyzwitterion (PZ); ( $k_0$  = rate constant without added electrolyte).  $[\text{Fe}(\text{CN})_6^{4-}] = 1 \times 10^{-4} \text{ M}$ ;  $[\text{S}_2\text{O}_8^{2-}] = 3 \times 10^{-3} \text{ M}$ . The sign ↑ corresponds to the lower limit of  $k$  (solution in equilibrium with a precipitated phase)



**Figure 4** Variation of the intrinsic viscosity of the polyzwitterion in the presence of each salt of reaction (A) at different concentrations: (●)  $\text{Fe}(\text{CN})_6^{4-}$ ; (○)  $\text{S}_2\text{O}_8^{2-}$ ; (+)  $\text{Fe}(\text{CN})_6^{3-}$ ; (×)  $\text{SO}_4^{2-}$ . The arrows show the way of transformation of the salts, the sign | their upper or lower limits of concentration during reaction (A)

concentration range ( $\leq 10^{-3} \text{ M}$ ) have to be stressed: similar effects actually occur only in a much higher concentration range ( $> 10^{-3} \text{ M}$ ) for the usual monovalent salts<sup>5,6,10,14</sup>. The variations of the PZ chain expansion during the reaction cannot be derived from the previous results, because of the simultaneous presence and of the competition of the four anionic species involved in the process. However, a rather expanded conformation may be safely assumed for the polyzwitterionic chain.

The reaction system in presence of the model polyelectrolyte PE shows a very different behaviour. For  $[\text{PE}] > 10^{-4} \text{ M}$ , as soon as the salts for reaction (A) are added, the PE solution becomes cloudy. After a few minutes the precipitate separates and the spectral measurements are carried out on the supernatant clear

**Table 2** Pseudo-first order initial rate constants of the anion–anion reaction (A) in the presence of a small sulfobetaine molecule Z and a model polyelectrolyte PE at various concentrations:  $[\text{Fe}(\text{CN})_6^{4-}] = 1 \times 10^{-4} \text{ M}$ ,  $[\text{S}_2\text{O}_8^{2-}] = 3 \times 10^{-3} \text{ M}$

Additive	Concentration (M) ( $\times 10^5$ )	Rate constant $k$ ( $\text{min}^{-1}$ ) ( $\times 10^3$ )
	0	1.4
Z	10	1.4
Z	$10^3$	0.9
PE	1.0	15.0
PE	10	> 360
PE	$10^2$	> 1700

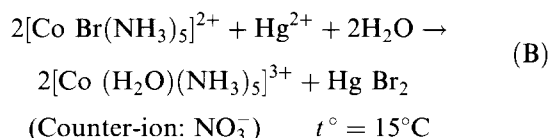
**Table 3** Pseudo-first order initial rate constants of the cation–cation reaction (B) in the presence of the polyzwitterion at various concentrations. Kinetic equation:  $f(\tau) = \ln(1 - d/\epsilon C_0) = kt$  [ $\text{CoBr}(\text{NH}_3)_5^{2+}] = 1 \times 10^{-5} \text{ M}$ ;  $[\text{Hg}^{2+}] = 3 \times 10^{-4} \text{ M}$ ;  $[\text{HNO}_3] = 1 \times 10^{-3} \text{ M}$

[PZ] (M)	Rate constant $k$ ( $\text{min}^{-1}$ )
0	$1.6 \times 10^{-2}$
$10^{-4}$	$1.4 \times 10^{-2}$
$10^{-3}$	$1.6 \times 10^{-2}$

solution. However, even in these heterogeneous conditions, as seen in *Table 2*, the measured rate constant, which is strongly underestimated, is clearly higher than that measured at the same overall concentrations of PZ and has to be estimated as a lower limit. A more accurate and corroborating result is obtained at  $10^{-5} \text{ M}$ , where no precipitation occurs. It may be noticed that this ‘salting-out’ effect, although classical for PEs, is actually observed in our case at a very low PE concentration ( $10^{-4} \text{ M}$ ,  $3.7 \times 10^{-3} \text{ g dl}^{-1}$ ), while for similar reacting ions concentration, the reacting medium apparently remains homogeneous for the cationic PE polybrene (1,5-dimethyl-1,5-diazaundecamethylene polymethobromide) up to very high concentrations (0.1 M,  $3.7 \text{ g dl}^{-1}$ )<sup>20</sup>. This striking difference may arise from the chemical structure (less hydrophilic counter-ion) and the very high molecular weight of the model PE. In any case, the soluble PE chains in the reacting medium show very likely a strongly collapsed conformation, in sharp contrast with the expanded chain of the polyzwitterion PZ.

Finally, as shown in *Table 2*, the low molecular weight sulfobetaine model Z does not induce any significant acceleration of reaction (1) and this typical feature emphasizes the polymeric and cooperative nature of the catalysis by PZ. The plot of  $k/k_0$  in *Figure 3* strikingly summarizes the respective importance of the addition of the three different ionic or zwitterionic species to the reacting medium.

#### Cation–cation reaction



Reaction (B) was monitored by following the fading of u.v. absorption of the bromopentaamminecobaltic reagent at  $254 \text{ nm}$ <sup>22</sup>. Because of its high molar extinction coefficient,  $1.67 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ , a low concentration

of  $1 \times 10^{-5} \text{ M}$  was used. The molar concentration of the mercuric salt being 30 times higher, pseudo-first order kinetics could be assumed and checked by using equation (1): during approximately the first 20 min (up to 30% of conversion) the plot for reaction (B) is strictly linear, whatever may be the value of the initial absorption  $d_0$ , which can then be set arbitrarily to zero. The absolute value of the initial negative slope of the kinetic curve represents the initial rate constant  $k$  of reaction (B) mentioned in *Table 3*. Within the limits of experimental errors, no significant differences between the rate constants in the absence or the presence of the polyzwitterionic additive can be found.

## DISCUSSION

A large amount of experimental evidence for the perturbation of the kinetics or the chemical equilibria of inter-ionic reactions in aqueous solution by addition of various electrolytes or PEs may be found in the literature<sup>15,16,18,19,30–32</sup>. The case of a PE added to a solution, where ions of the same sign, but opposite to the sign of the PE, are reacting, has been treated by the Manning theory<sup>33–35</sup>, which supposes the empirical assumption relating the acceleration of the reaction to an environmental effect in the vicinity of the PE chain, i.e. electrostatic attraction between the reaction ions and the charged sites on the polymer. More precisely, Morawetz and Shafer<sup>15,36</sup> and Ise and Tabushi<sup>16,30</sup> attribute the modification of the kinetics to the confinement of the attracted reacting ions in the macro-ion domain defined by the Debye–Hückel reciprocal shielding length  $\kappa^{-1}$ <sup>37–39</sup>: within this domain the electrostatic potential reaches a very high value, allowing thus a drastic enhancement of the inter-ionic collision probability. From a thermodynamic point of view, Ise and Tabushi relate the modified rate constant to electrostatic stabilization<sup>16,40</sup> and to the dehydration<sup>16,30</sup> of the activated complex between the reacting ions in the neighbourhood of the macro-ion.

Several more specific influences on the kinetics of the inter-ionic reactions catalysed by the PE have been discussed. In our case, the following effects can be safely excluded:

- hydrophobic or hydrogen bonding contributions<sup>15,16</sup>, because of the chemical nature of the reagents;
- solution viscosity effect (eventually due to the very high molecular weight of the PZ), as discussed by Morawetz<sup>15</sup>. This assumption is checked by the experimental fact that in our case a decrease of  $k$  was never observed after addition of the PZ to the ionic reacting medium.

Some of these ‘catalytic’ properties of polyelectrolytes may be more or less expected for PZs because of their common macromolecular nature and of the common presence of charged sites. However, a close analogy may be *a priori* ruled out. The inability of ion dissociation within the covalently bound zwitterionic moiety (which is indeed the essential difference with PEs) imparts to the PZ a unique set of properties (e.g. the ‘antipolyelectrolyte’ behaviour), which cannot be considered as a single balance between polyanion and polycation properties.

Thus, several factors can simultaneously increase or

decrease the rate constant  $k$  of the inter-ionic reaction and then competing influences have to be discussed.

The catalytic efficiency of PZ on the interanionic reaction between  $\text{Fe}(\text{CN})_6^{4-}$  and  $\text{S}_2\text{O}_8^{2-}$  is obvious and its macromolecular specificity is evidenced by the inefficiency of the sulfobetainic low molecular weight model molecule. The rate constant is strongly dependent on the ratio  $r = [\text{PZ}]/[\text{ionic reagents}]$ . At low  $r$  values, the relative rate constants  $k/k_0$  ( $k_0$  = rate constant in the absence of polymer additive) are weak and increase slowly, up to a threshold where the concentrations of zwitterionic sites and reacting ions in the whole reaction medium are of the same order of magnitude ( $10^{-3}$  M) (Figure 4). The fraction of reacting ions condensed on the PZ chain, in equilibrium with free ions in the solution, is obviously a complex function of their concentration, their binding constants to the polymer chain and the PZ concentration. These competitive bindings cannot be quantified, even if the much higher persulfate concentration and its apparent higher binding constant, as derived from its stronger influence on the PZ chain expansion, suggest preferential condensation of the reacting ions. In any case, it is clear that the PZ concentration has to reach some critical value in order that a significant fraction of both ions becomes actually bound to the chain, resulting in a measurable rate enhancement. The resulting variation of  $k/k_0$  versus the added polymer concentration is similar to that observed in typical ionic systems catalysed by PE<sup>26,41</sup>. However, in our case, a possible maximum of the curve (corresponding to a distribution of reacting ions over too many chains) cannot be observed for higher PZ concentrations because of the limited solubility of PZ.

It has to be noted that when the PZ is replaced by the model polyelectrolyte PE such a clear concentration threshold does not exist within the experimental concentration range (Figure 3): the catalysis already starts at very low concentrations.

The Debye-Hückel shielding length<sup>38</sup> may be calculated for the two systems according to

$$\kappa^{-1} = \left[ \frac{0.235886\epsilon}{\sum cZ^2} \right]^{0.5} \text{ (Å) at } 25^\circ\text{C}$$

where  $\epsilon$  is the dielectric constant of the solvent (= 78.36), and  $c$  and  $Z$  are the concentration and the charge of each free ion in the solution, respectively. The  $\kappa^{-1}$  values, 30.4 Å for the PZ and 29.7 Å for the PE solutions are nearly identical: the two systems are similar with respect to free ion-ion interactions, but the driving force for ion condensation is quite different for PZ and PE. It is higher for coulombic ion-polyion interactions in the case of PE than for ion-dipole interactions in the case of PZ, resulting in a higher 'catalytic' efficiency.

On the other hand, the strongly different polymer chain conformations in the medium (widely expanded for PZ as opposed to rather collapsed for PE) can also play a significant role in the process: the more widespread distribution of the reacting ions may afford a negative contribution to the catalytic effects.

The inter-ionic reaction in the presence of PZ shows autoretarded kinetics, as revealed by the significant decrease of the rate constant  $k$  at high conversions, and the transition between the two regimes is drawn towards higher conversion by increasing the PZ concentration.

This typical feature suggests competing binding of the reaction products, more especially of the ferricyanide anion, which apparently shows the strongest affinity for the PZ as derived from its strongest influence on the chain expansion (see above).

In the case of the inter-cationic aquation reaction of the bromopentaamminecobalt complex (where the calculated  $\kappa^{-1}$  value is enlarged to 70 Å with respect to the anionic reaction), the experimental results clearly show that the process is not accelerated by the PZ, while PEs such as sodium polystyrenesulfonates are well known for their catalytic behaviour, in fairly similar concentration range<sup>15,16,26,27,30,41</sup>. This typical feature suggests that binding of the two reacting cations by the zwitterionic chain is inefficient. It may be recalled that most of the studies related to ion-PZ interactions in dilute aqueous solution point out preferential binding of bulky and polarizable anionic species with respect to small cations characterized by a large hydration shell<sup>1,5,8,10</sup>; however, this well ascertained trend cannot be directly transposed to the system under study which precisely involves bulky and polarizable cationic species. No definite and reliable explanation can be now proposed for the striking difference between the PZ and the PE behaviours.

## CONCLUSIONS

It results from our study on a particular, but representative PZ, we chose for the grounds mentioned above, that it apparently acts like a weak polycationic catalyst towards a well known inter-anionic reaction, keeping nevertheless the specific zwitterionic properties, different from that of PEs, i.e. higher chain expansion and higher solubility by increasing ionic strength as shown by viscosity measurements. The whole catalytic behaviour may be accounted for by several factors, as it appears in the discussion of the results, but no experimental fact is able to distinguish a clearly overwhelming factor for each result. Only a comparative study including PZs with significantly different geometric and electrostatic structures and various ionic reagents may lead to a better understanding of the catalytic process, especially of the influence on catalysis of the zwitterionic chain expansion resulting from salt addition.

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## REFERENCES

- 1 Salamone, J. C. and Rice, W. C. 'Encyclopedia of Polymer Science and Engineering', 2nd Edn. Vol. 11, Wiley-Interscience, New York, 1988, p. 514
- 2 Hart, R. and Timmerman, D. *J. Polym. Sci.* 1958, **28**, 638
- 3 Rohm & Hass Co. *Br. Patent* 1077772, 1967
- 4 Monroy-Soto, V. M. and Galin, J. C. *Polymer* 1984, **25**, 121
- 5 Itoh, Y., Abe, K. and Senoh, S. *Makromol. Chem.* 1986, **187**, 1691
- 6 Schulz, D. N., Peiffer, D. G., Agarwal, P. K., Larabee, J., Kaladas, J. J., Soni, L., Handwerker, B. and Garner, R. T. *Polymer* 1986, **27**, 1734

- 7 Salamone, J. C., Volksen, W., Israel, S. C., Olson, A. P. and Raia, D. C. *Polymer* 1977, **18**, 1058
- 8 Salamone, J. C., Volksen, W., Olson, A. P. and Israel, S. C. *Polymer* 1978, **19**, 1157
- 9 Salamone, J. C., Tsai, C. C., Olson, A. P. and Watterson, A. C. *Adv. Chem. Ser.* 1980, **187**, 337
- 10 Monroy-Soto, V. M. and Galin, J. C. *Polymer* 1984, **25**, 254
- 11 Wielema, T. A. and Engberts, J. C. F. *N. Eur. Polymer J.* 1987, **23**, 947
- 12 Huglin, M. B. and Rego, J. M. *Macromolecules* 1988, **24**, 2556
- 13 Zheng, Y. L., Knoesel, R. and Galin, J. C. *Polymer* 1987, **28**, 2297
- 14 Knoesel, R., Ehrmann, M. and Galin, J. C. *Polymer* 1993, **34**, 1925
- 15 Morawetz, H. 'Macromolecules in Solution', 2nd Edn, Interscience, New York, 1975, p. 478
- 16 Ise, N. and Tabushi, I. 'An Introduction to Speciality Polymers', Cambridge University Press, Cambridge, UK, 1983, p. 49
- 17 Holluta, J. and Herman, W. *Z. Phys. Chem. (Leipzig)* 1933, **A166**, 453
- 18 Chlebek, R. W. and Lister, M. W. *Can. J. Chem.* 1966, **44**, 437
- 19 Kershaw, M. R. and Prue, J. E. *Trans. Faraday Soc.* 1967, **63**, 1198
- 20 Enokida, A., Okubo, T. and Ise, N. *Macromolecules* 1980, **13**, 49
- 21 Brönsted, J. N. and Livingston, R. *J. Am. Chem. Soc.* 1927, **49**, 435
- 22 Olson, A. R. and Simonson, T. R. *J. Chem. Phys.* 1949, **17**, 1167
- 23 Posey, F. A. and Taube, H. *J. Am. Chem. Soc.* 1957, **79**, 255
- 24 Morawetz, H. *Svensk Kem. Tidskr.* 1967, **79**, 309
- 25 Ise, N. and Matsui, F. *J. Am. Chem. Soc.* 1968, **90**, 4242
- 26 Morawetz, H. and Vogel, B. *J. Am. Chem. Soc.* 1969, **91**, 563
- 27 Ise, N. and Matsuda, Y. *J. Chem. Soc., Faraday Trans. 2* 1973, **69**, 99
- 28 Galin, M., Chapoton, A. and Galin, J. C. *J. Chem. Soc., Perkin Trans.* 1993, 545
- 29 Fuoss, R. M., Watanabe, M. and Coleman, B. D. *J. Polym. Sci.* 1960, **48**, 5.
- 30 Ise, N. *J. Polym. Sci., Polym. Symp.* 1978, **62**, 205
- 31 Brönsted, J. N. *Z. Phys. Chem. (Leipzig)* 1922, **102**, 169
- 32 Brönsted, J. N. *Z. Phys. Chem.* 1925, **115**, 337
- 33 Manning, G. S. *J. Chem. Phys.* 1969, **51**, 924
- 34 Manning, G. S. *Am. Rev. Phys. Chem.* 1972, **23**, 117
- 35 Ise, N. and Okubo, T. *Macromolecules* 1978, **11**, 439
- 36 Morawetz, H. and Shafer, J. A. *J. Phys. Chem.* 1963, **67**, 1293.
- 37 Debye, P. J. W. and Hückel, E. *Phys. Z.* 1923, **24**, 185
- 38 Armstrong, R. W. and Strauss, U. P. 'Encyclopedia of Polymer Science and Technology', Vol. 10, Wiley-Interscience, New York, 1969, p. 781
- 39 Amis, E. S. and Hinton, J. F. 'Solvent Effects on Chemical Phenomena', Vol. 1, Academic Press, New York, 1973, p. 207
- 40 Ise, N. *Adv. Polym. Sci.* 1970, **7**, 536
- 41 Vogel, B. and Morawetz, H. *J. Am. Chem. Soc.* 1968, **90**, 1368