

Complex formation between polyelectrolytes in dilute aqueous solution

Lee Webster and Malcolm B. Huglin*

Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, UK

and Ian D. Robb†

Unilever Research, Port Sunlight Laboratory, Bebington, Wirral L63 3JW, UK

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Polyelectrolyte complexes (PEC) have been formed from mixing dilute aqueous solutions of the polyanion poly[sodium (2-acrylamido-2-methyl propane sulfonate)] (PAMPSNa) with the polycations poly(4-vinylpyridinium chloride) (P4VPHCl) and poly(2-vinylpyridinium chloride) (P2VPHCl). Simultaneous conductometric and potentiometric titrations indicated the electrochemical endpoint of each titration. In all cases, the endpoint occurred at a unit molar ratio (UMR) of polyanionic to polycationic groups between 0.9 and 1.1 which means that titrations exhibit approximate 1/1 stoichiometry. Moreover, the position of the titrimetric endpoint was in good accord with the UMR at which PEC particles were observed to flocculate rapidly. It was found that endpoints were not affected by: (1) changing from P4VPHCl to P2VPHCl; (2) using P2VPHCl samples of different molecular weights; (3) the addition of salt to the titrant or (4) by raising the reaction temperature from 298 K to 323 K. Elemental analysis of precipitates revealed, however, that PEC were deficient in polyanionic units. Potentiometric titrations performed at different pH values yielded strong evidence that complex composition is dependent primarily upon the degree of ionization of polycationic groups in the system and to the conclusion that elemental analysis data emphasize deviations in complex composition which are not apparent from titrimetric results. Turbidimetric measurements showed that the PEC particles were large (compared to the wavelength range scanned) and did not change size significantly in the range of UMR measured. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Polyelectrolyte complexes (PEC) are formed by the electrostatic interaction of oppositely charged polyelectrolytes (PE) in solution¹. The formation of PEC is governed by the characteristics of the precursors, e.g. strength and position of ionic sites, charge density, and rigidity of polymer chains, as well as the chemical environment, such as solvent, pH, temperature, concentration etc.². Three different types of PEC have been prepared in water^{2–7}:

- (1) soluble PEC, i.e. macroscopically homogeneous systems containing small PEC aggregates,
- (2) turbid colloidal systems with suspended PEC particles in the transition range to phase separation,
- (3) two-phase systems of supernatant liquid and precipitated PEC which is readily separated and isolated as a solid after washing and drying.

One of the interests in reactions occurring between oppositely-charged synthetic polymers in solution lies in their similarity to biological systems³; moreover, those PEC which are insoluble have potential applications as,

for example, microcapsules, membranes and medical implants^{4–7}. It is apparent from the literature that the main aspects studied by different authors are the composition of PEC obtained under various experimental conditions and the stoichiometry of PEC reactions. In systems where insoluble PEC result, which this paper shall address, these features are often determined by elemental analysis of PEC precipitates and/or by combinations of conductometric, potentiometric and turbidimetric titration. The titrations are usually performed by the incremental addition of a solution of one PE to a solution containing the other precursor and are evaluated by assessing a titration endpoint (break or point of inflection) of the titration curve. A great deal of data regarding the stoichiometry and composition of PEC has been accumulated using these techniques, and, although the same types of PE combinations have often been studied, differences in preparation of polymer samples and in the procedures adopted for PEC formation and characterization have impeded the comparability of the results reported (cf refs 1, 2, 13, 14 and references therein). For example, Fuoss and Sadek⁸ in 1949 described the turbidimetric titration of poly(vinyl-*N-n*-butyl pyridinium bromide) with Napolyacrylate and sodium poly(styrene sulfonate) (PSSNa), which yielded non-stoichiometric PEC. On the other hand, comprehensive investigations dealing

* To whom correspondence should be addressed

† Present address: Centre for Water Soluble Polymers, North East Wales Institute, Mold Road, Wrexham, Clwyd LL11 2AW, UK

with the formation and structure of PEC from PSSNa and poly(vinyl-benzyl-trimethyl ammonium chloride) (which is a similar PE to poly(vinyl-N-*n*-butyl pyridinium bromide)) have been made by Michaels and his group⁹⁻¹³ who reached different conclusions. Michaels *et al.* used conductometric titrations and elemental analysis to show that 1/1 stoichiometry occurred in precipitates formed from mixing dilute ($< 2.0 \text{ g dm}^{-3}$) salt-free aqueous polymer solutions (irrespective of relative polyanionic/polycationic feed ratios and order of addition); deviations from 1/1 stoichiometry were observed, however, in acid-base PE titrations or when low molecular mass salts were present^{10,12,13}. Similarly, Philipp *et al.*¹⁴ have used turbidimetry, potentiometry and conductometry to investigate the influence of charge density and molecular geometry on PEC composition. Conductometric and potentiometric endpoints were generally found to occur at the same point, whereas significant differences between the electrochemical and turbidimetric endpoints were observed in systems where highly branched PE were used. It is apparent, therefore, that a clarification of the principal chemical and physical factors involved in PEC formation is required.

Previously¹⁵, the authors reported on the reaction stoichiometry of PEC formed by mixing poly[sodium(2-acrylamido-2-methyl propane sulfonate)] (PAMPSNa) (the salt of a strong polyacid) and poly(4-vinylpyridinium chloride) (P4VPHCl) (the salt of a weak polybase) in dilute aqueous solution. Gravimetric analysis of PEC in conjunction with u.v. analysis of supernatant liquids revealed that for many feed mixtures, PEC were non-stoichiometric; i.e. PEC contained more of the polycationic precursor than the polyanionic one and weights of precipitates were not in accord with those calculated on a stoichiometric basis. Moreover, deviations from 1/1 stoichiometry were greater when PAMPSNa was titrant, than for the reverse order of addition.

In the present paper, the investigation of PEC stoichiometry is now extended to examine the relevance of other possible system variables, specifically: (1) the position of the pyridinium group, viz. changing from P4VPHCl to poly(2-vinylpyridinium chloride) (P2VPHCl); (2) the molecular weights of polyelectrolyte precursors; (3) the presence of added salt; (4) the temperature at which titrations were performed; and (5) the pH of the reaction medium. Using data from potentiometric and conductometric titrations as well as gravimetric analysis of PEC precipitates, it is the intention of the authors to ascertain the cause of deviations from 1/1 stoichiometry reported previously in this particular system.

CONDITIONS AND ABBREVIATIONS

Unless denoted specifically otherwise, the relevant temperature is 298 K. Also the molarities (M) of PE mean mol of sub-units per dm^3 . The concentration of solutions is 5×10^{-3} M and, in order to minimize volume changes during titrations, that of the titrants is 0.1 M.

The unit molar ratio (denoted UMR) is the ratio of moles of sub-units of the titrant PE to the number of moles of sub-units of the other polyelectrolyte in the reaction mixture at any stage during the titration. Because the titrant can be anionic or cationic, the UMR values quoted in the text may represent both orders of addition.

EXPERIMENTAL

Materials

The polysalts PAMPSNa and P4VPHCl were prepared and characterized using the methods described previously¹⁵.

Samples of poly(2-vinylpyridine) (P2VP) of quoted molar mass $0.4 \times 10^5 \text{ g mol}^{-1}$ (denoted P2VP-1) and $3 \times 10^5 \text{ g mol}^{-1}$ (P2VP-2) were purchased from Polyscience Ltd. The poly(2-vinylpyridinium chloride) salts (P2VPHCl-1 and P2VPHCl-2) were prepared as for P4VPHCl and were found to be 96% and 95% quaternized, respectively. The poly(vinylpyridinium chloride) samples (collectively denoted PVPPhCl) had a pH of *ca.* 2 in water at 0.1 M concentration.

Methods

Conductometric and potentiometric titrations. Conductometric titrations were performed using an S & M AGB-77 conductivity meter and pH measurements were made using an EDT RE 357 pH meter. Conductance and pH of the mixed solutions were measured at various unit mol ratios; reproducibility was found to be within 2%. The reactions were carried out by slow dropwise addition of titrant via an Agla microsyringe to the solution with rapid stirring. The solutions were maintained at constant temperature in a thermostated water bath. Before mixing, the individual solutions were clear and colourless; upon mixing, turbidity developed immediately. After a certain volume of titrant had been added to each solution, the white, solid products flocculated rapidly to yield a precipitate and a clear supernatant liquid. PVPPhCl salts are more acidic in aqueous solution than PAMPSNa, and because changes in pH during titration affect the conductance of the reaction mixture, it is expedient to measure both pH and conductance together.

Gravimetric analysis of PEC. The composition of PEC precipitates formed during conductometric/potentiometric titrations was evaluated by gravimetric analysis. PE were mixed in the following UMR: 0.30, 0.70, 1.00, 1.20 and 1.50. Precipitates from each reaction were isolated via centrifugation, washed repeatedly with deionized water until all ions not associated with PEC were removed and finally dried to constant mass *in vacuo* at 343 K.

The weight percentage of sulfur in PEC was found from elemental analysis and used to calculate the weight of 2-acrylamido-2-methyl propane sulfonate units (AMPS^-) in complexes and subsequently the mole fraction of AMPS^- (X_{AMPS^-}) present in each PEC. The mole fraction of 4-vinylpyridinium units (4VPH^+) was obtained by difference. Samples were also subjected to elemental analysis to obtain the wt% of chlorine and sodium in PEC.

Turbidimetric measurements. Turbidimetric measurements were made at 2 nm intervals between 400 and 625 nm using a Hewlett Packard 8452 spectrophotometer. After each addition of titrant to the reaction mixture, the solution was stirred at constant temperature for a minimum of 2 h. Turbidity was measured by sampling the reaction mixture directly into a 5 mm path length cell; care was taken to ensure that the cell was

maintained ± 0.1 K of the temperature of the reaction mixture. The turbidity of some samples was measured after 24 h, 3 days and 1 week had elapsed to ascertain if turbidity remained constant.

RESULTS AND DISCUSSION

Conductometric and potentiometric titrations

The use of conductance measurements to examine the reaction between oppositely-charged polyions depends on the change in concentration of species of different equivalent conductance¹³. Conductometric titration techniques have been used by other workers^{2,9-14,16-21} to investigate the stoichiometry of PEC formation between polyelectrolytes. For example, Tsuchida^{2,16} has shown that, in titrations between two polysalts, conductance rises at a constant rate to the endpoint due to the release of small, mobile counterions into solution. After the endpoint, there is no further release of counterions and the excess of titrant comprises PE. Hence, the resultant rise in conductance becomes less rapid. The endpoint of reaction is clearly observed therefore as an inflexion point on the conductance curve and the ratio of anionic to cationic units (or vice versa) may be calculated accordingly.

(a) *Incremental addition of PAMPSNa to PVPHCl.* Regarding the present work, Figures 1–3 show the results of conductometric and potentiometric titrations for the addition of PAMPSNa to PVPHCl. The UMR at which the flocculation of PEC was observed is marked on each figure. The following features are of note:

- (1) conductance falls slowly during titration until, in the region of the endpoint, the slope of the graph falls rapidly. After the endpoint, the conductance begins to rise very slowly;
- (2) the pH of the solution rises steadily during titration. The pH rises more quickly in the region of the endpoint;
- (3) the plots show that the endpoints occur at $UMR \approx 1/1$;
- (4) the shapes of the titration curves are not affected by changing from P4VPHCl to P2VPHCl (Figures 1 and 2) or by changing the molecular weight of the P2VPHCl component (Figures 2 and 3);

The shape of the potentiometric titration curves offers a considerable insight into the mechanism of PEC formation in this system and can be explained as follows by considering a specific case, e.g. Figure 1.

Since P4VPHCl is the salt of a weak polybase and a strong acid, the pH of the 5×10^{-3} M P4VPHCl solution initially, i.e. at the start of the titration, would be expected to be < 7 . In fact, the value is 2.75. At pH 2.75, not all of the 4-vinylpyridine (4VP) units will be ionized to 4-vinylpyridinium (4VPH⁺) sites, because the pK_a value of P4VP is 4.2²². Approximately 4% of groups would be expected²³ to be uncharged at this pH (although the exact percentage is uncertain due to the polyelectrolyte effect where the neighbouring charges make further ionization more difficult²³). Unionized 4VP units are unable to participate in coulombic interaction with anionic sulfonate (AMPS⁻) moieties. Consequently, as the titration proceeds, PEC is formed with

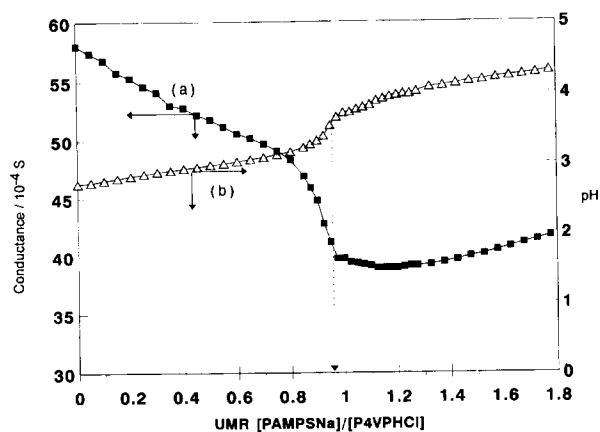


Figure 1 Conductometric (a) and potentiometric (b) curves for the incremental addition of PAMPSNa to P4VPHCl. The flocculation point is indicated by the vertical dotted line

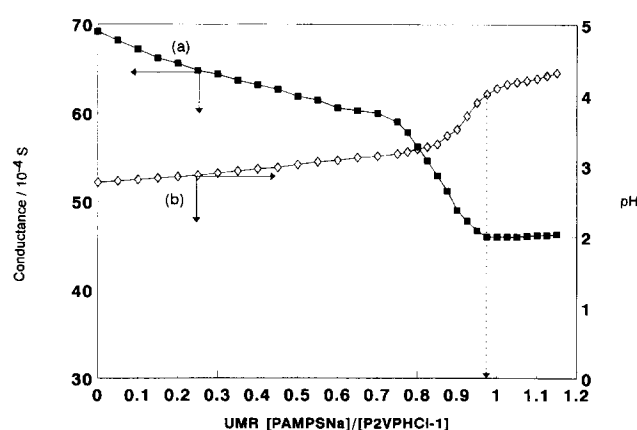


Figure 2 Conductometric (a) and potentiometric (b) curves for the incremental addition of PAMPSNa to P2VPHCl-1. The flocculation point is indicated by the vertical dotted line

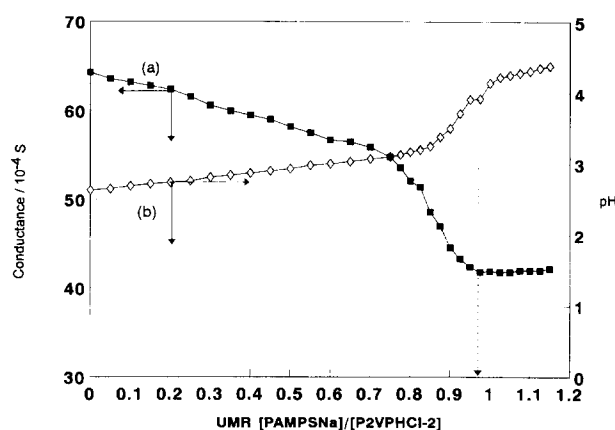


Figure 3 Conductometric (a) and potentiometric (b) curves for the incremental addition of PAMPSNa to P2VPHCl-2. The flocculation point is indicated by the vertical dotted line

some of the 4VP groups present in the unionized form. The coulombic bonds between the ionized 4VPH⁺ and RSO₃⁻ present in the complex, however, lower the positive charge density around the unionized 4VP units which in turn facilitates the ionization of 4VP groups. This ionization occurs, causing H⁺ from the solution to be consumed; the pH of the solution rises and, because the conductivity of H⁺ ions is at least three times greater

than that of the counterions released into solution²⁴, the conductance of the solution falls simultaneously. Note that: (1) the solution volume remains practically unchanged by the addition of titrant and thus the pH change observed here must be due in part to the ionization of 4VP groups present in the system (see the explanation later to *Figures 6* and *7*, which presents further evidence of ionization of previously uncharged groups) and (2) because PAMPSNa is the salt of a strong acid and a strong base it is considered to be 100% ionized in the pH range considered in this work.

The endpoint of this titration is observed when the complexation between PAMPSNa and P4VPHCl is complete; before the endpoint is reached, the PEC particles are homogeneously distributed in the solution due to the presence of repulsive positive charges (from the excess P4VPHCl). At the endpoint, i.e. at charge neutralization of the dispersed phase, flocculation occurs as the charge barriers are removed. Immediately prior to flocculation, some of the remaining unionized 4VP units are ionized and the pH of the solution rises rapidly. Accordingly, the conductance falls also. The flocculation point and the electrochemical endpoints are observed at $UMR = 0.95$ which indicates an approximately stoichiometric reaction. Note that accuracy in titrations is reduced primarily by the low purity of PE samples; i.e. P4VPHCl samples were only 96% quaternized. Hence, the authors agree with Phillip *et al.*¹⁴, who, when reviewing their work on PEC from mixing a wide range of PE, suggested that 1/1 PEC should encompass all complexes containing a molar ratio of anionic to cationic groups between 0.90 and 1.10. They asserted that deviations from 1/1 stoichiometry within this range may be apportioned to limitations in reproducibility of preparation and characterization of PEC. The electrochemical endpoints suggest, therefore, that complexation is complete when equimolar amounts of each PE are present in the reaction mixture. The endpoints do not, however, give any indication that precipitates are rich in the polycationic component, although gravimetric analysis results presented in *Table 1* show unequivocally that PEC are deficient in PAMPSNa. This is an important point, especially because composition of precipitates is an important factor when assessing the potential of PEC as polymeric materials.

(b) *Incremental addition of PVPHCl to PAMPSNa.* *Figures 4* and *5* present the potentiometric and conductometric titration curves when PVPHCl is added to PAMPSNa. The endpoints are marked as for *Figures 1–3*. For each of these figures, the following features are of note:

- (1) the conductance rises steadily, until the endpoint is reached after which the conductance rises more quickly; and
- (2) pH falls rapidly at the start of titration, and again near the endpoint.

As with *Figures 1–3*, the shape of the potentiometric titration curves is significant with respect to the mechanism of PEC formation. The form of the curves can be explained by considering a specific example, e.g. *Figure 4*.

At the start of the titration, the pH of the PAMPSNa solution is 6.5 and the pH of the P4VPHCl solution in the burette is pH 2. Addition of titrant to PAMPSNa

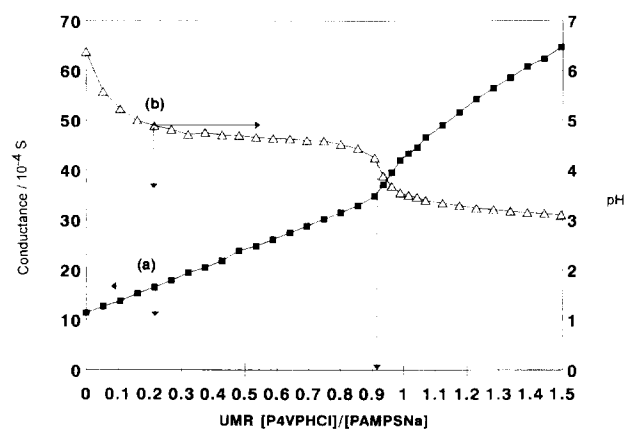


Figure 4 Conductometric (a) and potentiometric (b) curves for the incremental addition of P4VPHCl to PAMPSNa. The flocculation point is indicated by the vertical dotted line

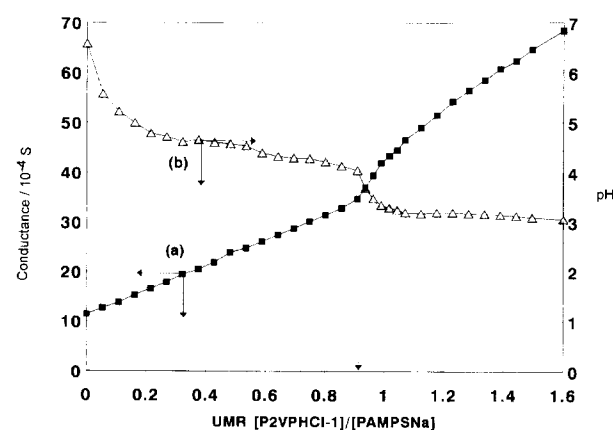


Figure 5 Conductometric (a) and potentiometric (b) curves for the incremental addition of P2VPHCl-1 to PAMPSNa. The flocculation point is indicated by the vertical dotted line

results in the simultaneous formation of PEC and, importantly, the rapid decrease in pH of the solution. This decrease in pH can only be due to the release of H^+ ions into solution which were previously associated with 4VP sites in the titrant. This means, therefore, that PEC are formed which contain unionized 4VP groups (N.B. The percentage of unionized groups present in PEC can be estimated at any time by considering the number of moles of acid required to reduce the pH of the solution from 6.5 at the start of the titration to pH 4 at the endpoint). Flocculation of PEC occurs at $UMR = 0.93$ which indicates an approximately stoichiometric reaction. In contrast to *Figures 1–3*, an increase in pH is not observed prior to flocculation. The authors suggest that at pH 4 there are insufficient protons available in the solution to effect the ionization of uncomplexed 4VP units (this point is discussed further in the notes to *Figures 6* and *7* below). After the endpoint, addition of excess titrant causes the pH of the solution to fall rapidly. Hence the electrochemical endpoint is considered to be at the start of the inflexion on the potentiometric titration curve. This endpoint is coincidental with flocculation of PEC.

(c) *Titrations between PAMPSNa and P4VPHCl performed at pH 3.* The results presented in parts (a) and (b) above strongly suggest that deviations from 1/1

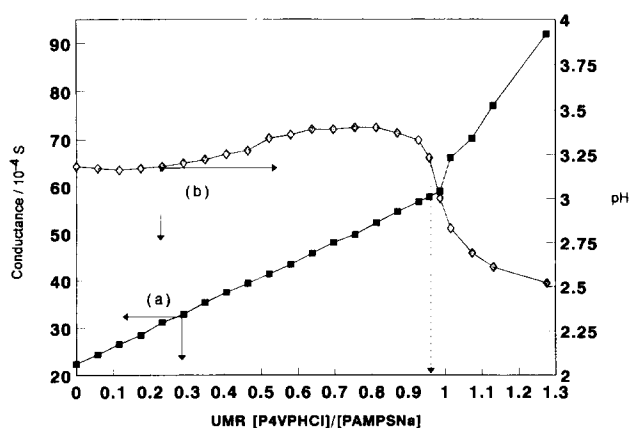


Figure 6 Conductometric (a) and potentiometric (b) curves for the incremental addition of P4VPHCl to PAMPSNa solution of initial pH reduced to 3.18. The flocculation point is indicated by the vertical dotted line

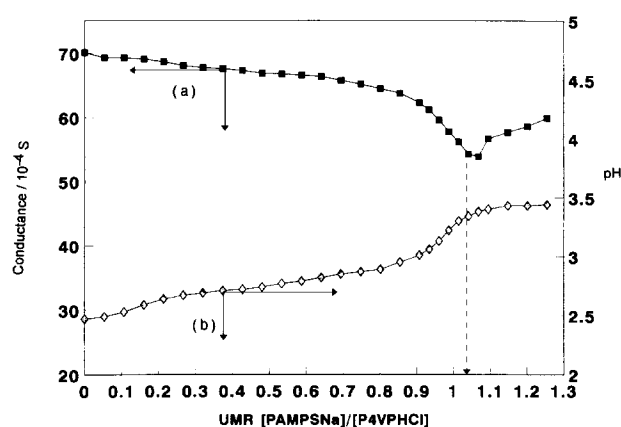


Figure 7 Conductometric (a) and potentiometric (b) curves for the incremental addition of PAMPSNa to P4VPHCl. The pH of the titrant (PAMPSNa) was reduced to 2.90 and the flocculation point is indicated by the vertical dotted line

stoichiometry in this system are due to the presence of unionized VP groups in precursor solutions and resultant PEC. Figures 1–3 show clearly that the pH of 5×10^{-3} PVPHCl solutions ≈ 3 . At pH 3 at least 90% of VP

groups are expected to be ionized to VPHCl. In order to investigate the effect of pH on the endpoints of conductometric/potentiometric titrations between PAMPSNa and P4VPHCl, two titrations were performed where the PAMPSNa solutions were acidified to $\text{pH} \approx 3$ with aqueous HCl. This pH value was chosen as it coincides with the pH of the 5×10^{-3} P4VPHCl precursor which should minimize pH changes during titrations. Figures 6 and 7 show the conductometric and potentiometric titration curves at this reduced pH. The potentiometric titration curves show that the pH of each solution rises to values above the pH of the individual precursors before the endpoint of the reactions are reached. This experimental observation provides strong evidence that 4VP units become ionized as the titration proceeds.

Gravimetric analysis of PEC

The composition of precipitates formed at different UMR, which was obtained previously from elemental analysis, was found to be dependent upon order of addition¹⁵ (see Table 1). The conductometric and potentiometric titration results reported here indicate that the deviations from 1/1 stoichiometry derived from elemental analysis results are due to the presence of unionized 4VP groups in the system. The composition of PEC is most likely therefore to be pH dependent, but another possible cause of deviations from 1/1 stoichiometry has been considered, viz. the high viscosity of the reaction mixture; i.e. PEC precipitation occurring before the polyelectrolytes were mixed sufficiently well. In order to test this hypothesis, two titrations were carried out where the viscosity of the system was reduced. In the first, the titration was performed at 333 K and in the second 0.1 M NaCl was added to the titrant as a means of lowering its viscosity. PAMPSNa was chosen as the titrant in both cases; firstly because this order of addition shows the greatest deviations from 1/1 stoichiometry¹⁵ and secondly because the PAMPSNa solutions used were significantly more viscous than the PVPHCl solutions. Flow times of 0.1 M PAMPSNa were determined in water at 298 K and 333 K and in 0.1 M NaCl at 298 K

Table 1 PEC compositions determined from elemental analysis

(a) Incremental addition of P4VPHCl to PAMPSNa

UMR [P4VPHCl]/[PAMPSNa]	wt. %S in complex ± 0.3	X_{AMPS^-} in complex ± 0.02	X_{4VPH^+} in complex ± 0.02
0.30	9.1	0.40	0.60
0.70	9.1	0.40	0.60
1.00	9.3	0.44	0.56
1.20	9.7	0.46	0.54
1.50	9.1	0.40	0.60

(b) Incremental addition of PAMPSNa to P4VPHCl

UMR [PAMPSNa]/[P4VPHCl]	wt. %S in complex ± 0.3	X_{AMPS^-} in complex ± 0.02	X_{4VPH^+} in complex ± 0.02
0.30	7.3	0.31	0.69
0.70	7.7	0.35	0.65
1.00	7.4	0.32	0.68
1.20	7.5	0.33	0.67
1.50	7.6	0.34	0.66

Table 2 PEC compositions determined from elemental analysis

(a) Incremental addition of PAMPSNa to P4VPHCl at 333 K			
UMR [PAMPSNa]/[P4VPHCl]	wt. %S in complex ± 0.3	X_{AMPS^-} in complex ± 0.02	$X_{\text{4VP}^{\text{H}^+}}$ in complex ± 0.02
0.30	6.9	0.28	0.72
0.70	7.0	0.28	0.72
1.00	7.1	0.30	0.70
1.50	6.7	0.28	0.72
(b) Incremental addition of PAMPSNa in 0.1 M NaCl to P4VPHCl at 298 K			
UMR [PAMPSNa]/[P4VPHCl]	wt. %S in complex ± 0.3	X_{AMPS^-} in complex ± 0.02	$X_{\text{4VP}^{\text{H}^+}}$ in complex ± 0.02
0.30	7.2	0.31	0.69
0.70	7.4	0.33	0.67
1.00	7.1	0.31	0.69
1.50	6.8	0.28	0.72

Table 3 Compositions determined from elemental analysis of PEC produced from PE solutions of pH ~ 3

(a) Incremental addition of P4VPHCl to PAMPSNa			
UMR [P4VPHCl]/[PAMPSNa]	wt. %S in complex ± 0.3	X_{AMPS^-} in complex ± 0.02	$X_{\text{4VP}^{\text{H}^+}}$ in complex ± 0.02
0.130	9.4	0.44	0.56
0.70	9.3	0.44	0.56
1.00	9.1	0.40	0.60
1.20	9.1	0.40	0.60
1.50	9.1	0.40	0.60
(b) Incremental addition of PAMPSNa to P4VPHCl			
UMR [PAMPSNa]/[P4VPHCl]	wt. %S in complex ± 0.3	X_{AMPS^-} in complex ± 0.02	$X_{\text{4VP}^{\text{H}^+}}$ in complex ± 0.02
0.30	9.0	0.40	0.60
0.70	8.9	0.40	0.60
1.00	9.1	0.40	0.60
1.20	9.4	0.44	0.56
1.50	9.3	0.44	0.56

using an Ubbelohde suspended level viscometer. The relative viscosities (η_r) were not corrected for possible influence of finite rate of shear, which is not expected to be significant at moderate values of η_r . A decrease of 3.2 in the apparent value of η_r from that in water at 298 K ($\eta_r = 11.8$) occurs both in water at 333 K and in aq. NaCl at 298 K. Although these reductions are not dramatic, they are nonetheless significant. It was found, however, that PEC composition was not affected by either the increase in temperature of the system or the addition of salt to the titrant (see *Tables 2a* and *b*).

Table 3 gives the PEC compositions found from elemental analysis of precipitates formed at pH ≈ 3 . All PEC have a slight excess of the polycationic (4VP) component, but *Table 3* reveals that order of addition is not a significant factor in PEC composition at this pH.

An interesting observation with respect to all elemental analysis results reported here is that elemental analysis of PEC did not detect any Na^+ or Cl^- ions. This has implications with regard to the accuracy of PEC compositions; mole fractions were calculated originally¹⁵

on the basis that complexes do not contain any small counterions. A source of error in the calculations, therefore, was expected to be the presence of sodium and chloride ions bound to uncomplexed PE units. It is extremely unlikely (for steric reasons) that all charged sites are able to form coulombic bonds, and electrical neutrality in PEC must be maintained therefore, not by Na^+ or Cl^- but H^+ or OH^- counterions wherever necessary. This means that errors due to the presence of small counterions cannot be estimated from elemental analysis. Fortunately, however, errors due to the presence of H^+ and OH^- in PEC are expected to be negligible due to the small mass of these units relative to the mass of PE sub units.

The titrimetric and gravimetric results reported here, in conjunction with findings reported elsewhere²⁵ on the difficulties encountered when attempting to protonate the weak polybase, poly(vinylpyridine), completely, lead to the conclusion that the excess 4VP groups found in PEC here and previously¹⁵ are due to the presence of unionized VP groups in both the precursor solutions and

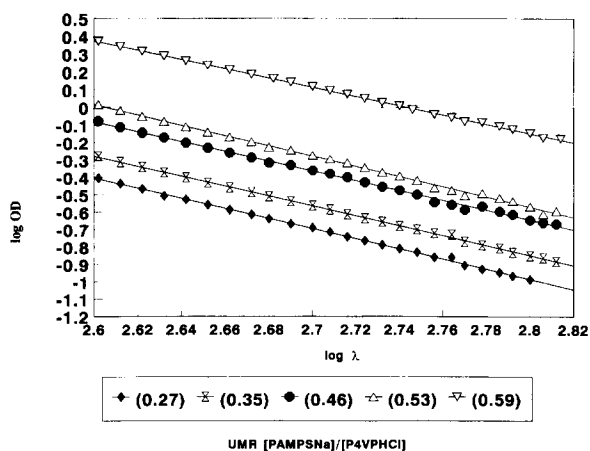


Figure 8 Curves of log OD vs log λ for the incremental addition of PAMPSNa to P4VPHCl

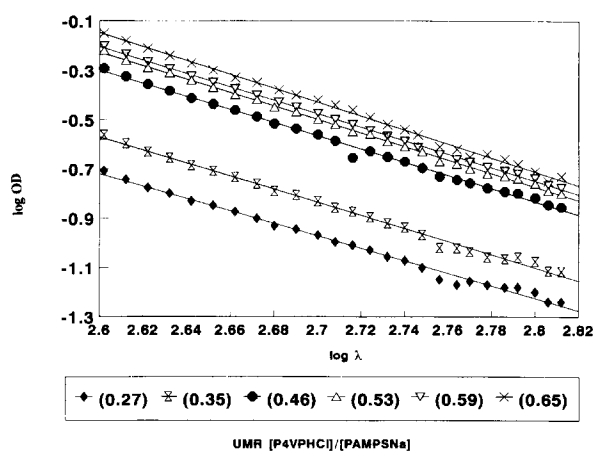


Figure 9 Curves of log OD vs log λ for the incremental addition of P4VPHCl to PAMPSNa

reaction mixtures. In this work one of the PE is strongly acidic, but we re-emphasize the critical relevance of the weakly basic nature of the other PE used. Smid and Fish¹ have concluded from extensive published evidence that 1/1 stoichiometry is the norm in systems where the pK_a values are less than 2 for each precursor.

Another important conclusion drawn from this work is that the gravimetric analysis data highlight deviations from 1/1 stoichiometry far more than the titrimetric techniques used. The authors would like to stress, therefore, that certain phenomena, e.g. the influence of order of addition on composition of PEC, may have gone unnoticed if titrimetric methods had been used in preference to gravimetric analysis of precipitates.

TURBIDIMETRIC MEASUREMENTS

Turbidimetric titrations have been used to indicate the endpoint of PEC formation in a number of publications^{1,2,8,12,14}. In this work, however, turbidimetric measurements were taken in order to supplement results from conductometric and potentiometric titrations and gravimetric analysis, since flocculation of PEC was observed visually at the endpoint in conductometric and potentiometric titrations. The measurements were made specifically to ascertain if turbidity is dependent

upon order of addition and also to assess if particle size changes markedly as titrant is added to the reaction mixtures.

For non-absorbing spherical particles, Heller *et al.*²⁶⁻²⁹ have given the following generalized relationship for the specific turbidity of a sol as a function of the wavelength (λ) of light used

$$(\tau/c)_{c \rightarrow 0} = k\lambda^{-n} \quad (1)$$

where τ is the turbidity at concentration c , k is a constant and the value of the exponent n is a function of particle size and relative refractive index (particle/medium). For particles of diameter much smaller than the wavelength used ($< \lambda/10$), $n = 4$ (Rayleigh scattering). For larger particles, n decreases gradually and may be used therefore as an indication of particle size during titration. The value of n will also be sensitive to any flocculation occurring in the system. Assuming the independence of k on wavelength over the narrow range of λ considered³⁰, equation (1) yields

$$n = -(\partial \log \tau / \partial \log \lambda)_c \quad (2)$$

Practically we have used optical density (OD) as a measure of turbidity. The findings obtained for both orders of addition are shown in Figures 8 and 9 from which the following points are of note:

- (1) the slope of each plot remains fairly constant at *ca.* -3.0 . Consequently, from equation (2) above, n has an approximate value of 3 which means that PEC particles are large compared to the wavelengths scanned;
- (2) turbidity is greater when PAMPSNa is titrant;
- (3) the electrochemical endpoints were not reached in either titration due to the high turbidity of solutions produced.

Point (1) provides evidence that PEC particle size remains reasonably constant over the ranges studied—i.e. particles increase in number rather than size as precipitation proceeds—and that the particle size is of the same order of magnitude independent of order of addition. As a consequence, point (2) above provides important corroboration via an entirely different technique of the trends in PEC mass data obtained previously¹⁵, viz. the addition of PAMPSNa to PVPHCl yielded higher precipitate masses than when the order of addition was reversed. In addition, the turbidity of those samples which was measured after 24 h, 3 days and 1 week had elapsed was found to be constant.

The value of n can also be used to indicate the shape of particles which cause scattering. Oster³¹ quotes the relationship

$$\tau \propto \lambda^{-4+\beta} \quad (3)$$

where β equals zero for a Rayleigh scatterer. For larger particles, β equals 1.0, 1.74 and 2.0 for rods, coils and spheres respectively. When n equals 3, therefore, the particles causing scattering are rod-like. This observation is consistent with the 'ladder' model of PEC formation proposed by Michaels *et al.*¹³, although it is unlikely that PEC will form exactly in this ideal way.

In addition to the turbidimetric titrations described above, further titrations were performed with PAMPSNa as titrant in the presence of 0.1 M NaCl at 298 K and 333 K. In all cases, $n \approx 3$ up to the maximum UMR measured (UMR = 0.70). Furthermore, the

turbidity of solutions was lower in the presence of added salt due to the lowering of specific charge effects²⁸, but was not affected by the temperature of mixing. These findings corroborate those reported above i.e. the pH of the reaction mixtures has greater importance than the viscosity of the reaction mixtures with respect to the composition of PEC precipitates produced in this system.

In conclusion, therefore, the turbidimetric results yield interesting supplementary information on PEC formation between PAMPSNa and P4VPHCl especially with respect to the dependence of turbidity upon order of addition and the constancy of *n* values for all measurements made.

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