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Complex formation between poly(4-vinylpyridinium chloride) and poly[sodium(2-acrylamido-2-methyl propane sulfonate)] in dilute aqueous solution

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Polyelectrolyte complexes (PEC) have been formed by mixing dilute aqueous solutions of the oppositely charged polyelectrolytes poly[sodium(2-acrylamido-2-methyl propane sulfonate)] (PAMPSNa) and poly(4-vinylpyridinium chloride) (PVPHCl). Over the entire range of feed compositions examined, a compact precipitate resulted. For many feed compositions, gravimetric analysis of the complex coupled with ultraviolet analysis of supernatant liquids demonstrated departures from stoichiometry. It was established that the composition of the complex was dependent upon the order of mixing: when PVPHCl was added to PAMPSNa, complexes contained approximately equimolar quantities of each precursor, whereas the complex comprised a significantly greater ratio of polycationic to polyanionic units when the order of addition was reversed. PEC formation in the presence of added salts was investigated also. Non-reacting solutions having a total polymer concentration of 12.3 g dm^{-3} could be prepared in *ca.* 1.8 molal aqueous solutions of NaCl, NaBr and LiBr, but at lower salt concentrations PEC were formed due to insufficient shielding of ionic charges. Analysis of PVPHCl, PAMPSNa and PEC via differential scanning calorimetry and nuclear magnetic resonance spectroscopy established glass transition temperatures for the precursors only. It was concluded that glass transition temperatures for the complexes could not be detected due to the high density of ionic crosslinking.

(Keywords: polyelectrolyte complex; poly[sodium(2-acrylamido-2-methyl propane sulfonate)]; poly(4-vinylpyridinium chloride); u.v. absorbance; stoichiometry)

INTRODUCTION

Polyelectrolyte complexes (PEC) are formed by the electrostatic interaction of oppositely charged polyelectrolytes (PEL) in solution[1]. The formation of PEC is governed by the characteristics of the PEL components, 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 and concentration[2]. Reactions occurring between oppositely-charged synthetic polymers are of interest because of their similarity to biological systems[3]: PEC have potential applications as, for example, microcapsules, membranes and medical implants[5–7].

In previous papers[8,9] we reported on PEC formed upon mixing the basic polymers, poly(2-vinylpyridine) (P2VP) and poly(4-vinylpyridine) (P4VP), with the polyacid poly(2-acrylamido-2-methyl propane sulfonic acid) (PAMPS). When solutions of these polymers were mixed, precipitation occurred. The precipitation was non-stoichiometric, i.e. there were differences between the actual weights of the precipitates and the weights calculated on a stoichiometric basis, and also the precipitates did not contain equimolar amounts of each polyelectrolyte. Deviations from 1 : 1 stoichiometry upon mixing strong, synthetic PEL have been reported by other workers including Fuoss and Sadek[10], Philipp *et al.*[11] and Michaels and co-workers[12,13]. The third group observed 1 : 1 stoichiometry when poly[sodium-(styrene sulfonate)] and poly(vinylbenzene trimethylammonium chloride) were mixed but found that deviations from 1 : 1 stoichiometry occurred in free acid–free base PEC titration and/or in the presence of added salt[12]. The free acid–free base system is analogous to the PVP/PAMPS systems studied by us previously[8,9], except that the complexes in that case were prepared in ethanol/water mixtures [70/30 (v/v)] because both P2VP and P4VP are insoluble in water[8].

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In this paper, it is our intention to investigate PEC formation and reaction stoichiometry upon mixing the polysalts poly(4-vinylpyridinium chloride) (PVPHCl) and poly[sodium(2-acrylamido-2-methyl propane sulfonate)] (PAMPSNa) in dilute aqueous solution, utilizing information from PEC weights and PEC compositions determined from elemental and ultraviolet analyses of supernatant liquids.

EXPERIMENTAL

Materials

An aqueous solution of 2-acrylamido-2-methyl propane sulfonic acid (AMPS; Sigma Chemical Co.) in the presence of ammonium persulfate was outgassed with gaseous nitrogen for 1 h prior to polymerization at 323 K for 1 h, the initial concentrations of monomer and initiator being 0.483 mol dm^{-3} and 1×10^{-3} mol dm^{-3}, respectively. Unreacted monomer was removed by dialysis with bidistilled deionized water for 6 days, and PAMPS was obtained as a white powder by freeze-drying and final drying in a vacuum oven at 314 K for 2 days. The conversion was 60%. The molecular mass of 9×10^5 g mol^{-1} was determined from the limiting viscosity number measured in 4.5 M aqueous NaCl at 298 K in conjunction with the Mark–Houwink–Sakurada constants[14].

The polysalt, PAMPSNa, was prepared by dissolving PAMPS in water and neutralizing the acid groups with standardized aqueous NaOH. The solution was adjusted to a concentration of 0.1 mol-segment dm^{-3} (hereafter, all PEL concentrations are designated in terms of unit molar concentration, i.e. 0.1 mol-segment dm^{-3} becomes 0.1 M) by the addition of bidistilled deionized water. The pH of PAMPSNa solutions at this concentration is ~7.

P4VP of quoted molar mass 0.4×10^5 g mol^{-1} was purchased from Polyscience Ltd. This polybase was converted to the polysalt PVPHCl by the addition of a stoichiometric amount of standardized aqueous hydrochloric acid and adjusted to 0.1 M by the addition of bidistilled deionized water. PVPHCl was obtained as an off-white/yellow powder following freeze-drying and final drying in a vacuum oven at 314 K. The degree of quaternization of the polysalt was 98%, as determined by gravimetric analysis using the method of Kolthoff and Sandell[15].

Methods

Gravimetric analysis of PEC. Two series of PEC were prepared by mixing 0.1 M PAMPSNa and 0.1 M PVPHCl solutions. The mole fractions of VPHCl units in the feed (X_{VPHCl}) were 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80 and 0.90. In series 1, PVPHCl was added dropwise to PAMPSNa; in series 2, the order of addition was reversed. Before mixing, the individual solutions were clear and colourless; upon mixing, white precipitates formed immediately. The precipitates were isolated by centrifugation and washed repeatedly with bidistilled deionized water until all ions not associated with the individual complexes were removed. The PEC were dried to constant mass and analysed to determine precipitate compositions. 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 (see *Results and Discussion*). To examine stoichiometry under different reaction conditions, two further series of PEC were formed from mixing PAMPSNa and PVPHCl: in series 3, 0.1 M PVPHCl was added dropwise via an Agla microsyringe with rapid stirring at constant temperature (298 K) to 5×10^{-3} M PAMPSNa; in series 4, the order of addition (and concentration of solutions) was reversed. The mole fractions of titrant units (X_{titrant}) in the feed for both series were 0.23, 0.41, 0.50, 0.55 and 0.60. Precipitate mass data could not be obtained for series 3 and series 4, because the reduced concentration of the reaction mixtures led to very small weights of precipitates.

Ultraviolet (u.v.) analysis of supernatant liquids. In an attempt to corroborate PEC compositions from elemental analysis data, the supernatant liquids associated with each PEC from series 1 and series 2 were analysed by u.v. spectrophotometry using a Hewlett–Packard 8452 spectrophotometer. PVPHCl has an absorbance peak at 262 nm ($\lambda_{\max} = 262$ nm), at which wavelength PAMPSNa does not absorb. The absorbance of a series of standard solutions of PVPHCl, having concentrations between 10^{-4} and 10^{-6} M, was measured at this wavelength, and found to obey the Beer–Lambert law. The supernatant liquid and washings from each reaction were collected and made up to a known volume with bidistilled deionized water. From the concentration of PVPHCl detected in the supernatant liquids, it was possible, sometimes, to determine PEC composition.

PEC solubilities in salt–water solutions. The limiting compositions of various salt and water solutions in which equal amounts of PVPHCl and PAMPSNa could be dissolved without interacting were determined by measuring the solvent compositions at which PEC precipitation began to occur. A range of salts was used to determine if any one salt could shield ionic interactions significantly more efficiently than the others. Some measurements were repeated for mixtures containing a large excess of one PEL to ascertain if changing the feed compositions affected the solubility limits.

Differential scanning calorimetry (d.s.c.). D.s.c. measurements were made with a Mettler TA-3000 instrument, which was previously calibrated with indium. The glass transition temperatures (T_g) were determined using a heating rate of 10 K min^{-1} and the middle point criterion. In order to avoid differences in thermal history, all the samples were subjected to the same thermal treatment, i.e. 10 min at 423 K.

Nuclear magnetic resonance spectroscopy (n.m.r.). Glass transition temperatures for samples were elucidated from T_2 relaxation times at different temperatures using a Brooker MSL 300 instrument at a ^{1}H frequency of 300.13 MHz.

RESULTS AND DISCUSSION

Precipitate compositions and precipitate mass data

The precipitate compositions, determined from elemental analysis data, are summarized in *Tables 1* and *2*.

Table 1 PEC compositions determined from elemental analysis with both PEL solutions 0.1 M

X_{VPHCl} in feed	Wt% S in complex (±0.3)	$X_{\mathrm{AMPS^-}}$ in complex (±0.03)	$X_{\mathrm{VPH^+}}$ in complex (±0.03)
Series 1, PVPHCl titrant			
0.200	9.7	0.46	0.54
0.300	9.7	0.46	0.54
0.400	10.6	0.53	0.47
0.500	8.5	0.38	0.62
0.600	9.2	0.43	0.57
0.700	9.9	0.48	0.52
0.800	9.7	0.46	0.54
0.900	9.2	0.43	0.57
Series 2, PAMPSNa titrant			
0.200	4.2	0.16	0.84
0.300	5.6	0.23	0.77
0.400	6.7	0.28	0.72
0.500	7.0	0.30	0.70
0.600	6.7	0.28	0.72
0.700	6.7	0.28	0.72
0.800	7.0	0.30	0.70
0.900	7.3	0.31	0.69

Table 2 PEC compositions determined from elemental analysis with titrant 0.1 M and solution 5×10^{-3} M

X_{VPHCl} in feed	Wt% S in complex ±0.3	$X_{\mathrm{AMPS^-}}$ in complex (±0.03)	$X_{\mathrm{VPH^+}}$ in complex (±0.03)
Series 3, PVPHCl titrant			
0.230	9.1	0.40	0.60
0.410	9.1	0.41	0.59
0.500	9.3	0.44	0.56
0.550	9.7	0.46	0.54
0.600	9.1	0.40	0.60
Series 4, PAMPSNa titrant			
0.230	7.3	0.31	0.69
0.410	7.7	0.35	0.65
0.500	7.4	0.32	0.68
0.550	7.5	0.33	0.67
0.600	7.6	0.34	0.66

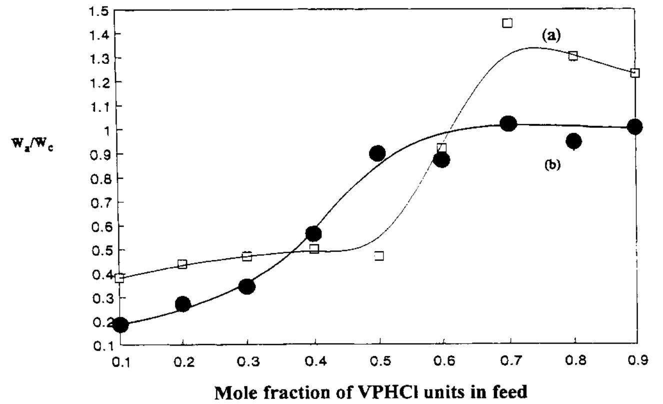

Figure 1 Change of W_a/W_c with X_{VPHCl} in feed when (a) PAMPSNa is titrant and (b) PVPHCl is titrant

PEC compositions were determined by assuming that complete stoichiometric reaction and total counterion release occurred. As an example, in the mixing of x moles of PVPHCl and y moles of PAMPSNa (where y is greater than x), the precipitate would contain x moles of each polyion, and the supernatant liquid would contain $(y-x)$ moles of PAMPSNa (the excess polyion) and x moles of NaCl (the moles of counterions released in a 1 : 1 pairing of oppositely-charged polyion functions), i.e.:

$$y \text{ PAMPSNa} + x \text{ PVPHCl} \rightarrow x \text{ PEC} + x \text{ NaCl} + (y-x) \text{ PAMPSNa} \quad (1)$$

Stoichiometry of 1 : 1 is observed when the mole fraction of AMPS$^-$ units in PEC is 0.5.

Note that the accuracy of the compositions determined using the above method is reduced if PEC are non-stoichiometric due to the fact that the precipitates must contain microions in order to maintain electrical neutrality. Furthermore, the weight percentages of sulfur in *Tables 1* and *2* have a quoted accuracy of ±0.3; i.e. a value of 10.0 wt%, for example, lies between 9.7 and 10.3%. For these reasons, the mole fractions of each polyelectrolyte contained in PEC have an estimate of experimental error attached of ±0.03.

Philipp *et al.*[11], when reviewing their work on PEC from mixing a wide range of PEL, suggested that 1 : 1 PEC should encompass all precipitates containing a molar ratio of anionic to cationic groups between 0.9 and 1.1, as deviations from 1 : 1 stoichiometry within this range may be apportioned to limitations in reproducibility of preparation and characterization of PEC. Using this classification, the data in *Tables 1* and *2* show that:

1. when PVPHCl is titrant, the PEC exhibit 1 : 1 stoichiometry or very slight deviations from it;
2. when PAMPSNa is titrant, PEC show large deviations from 1 : 1 stoichiometry;
3. the stoichiometry of reaction is not affected by changing the concentration of one solution from 0.1 to 5×10^{-3} M.

In addition, modifying the method of mixing to include rapid stirring and the addition of titrant in smaller aliquots did not affect reaction stoichiometry.

Reaction stoichiometry may also be described by comparing the actual weights of precipitates (W_a) with the weights calculated on a stoichiometric basis (W_c). *Figure 1* shows plots of W_a/W_c against feed composition for series 1 and 2. The plots show that:

1. when PVPHCl is titrant and $X_{\mathrm{VPHCl}} < 0.4$, $W_a/W_c < 0.6$;
2. when PVPHCl is titrant and $X_{\mathrm{VPHCl}} > 0.4$, W_a/W_c is approximately 1.0;
3. when PAMPSNa is titrant and $X_{\mathrm{VPHCl}} < 0.5$, $W_a/W_c < 0.5$;
4. when PAMPSNa is titrant and $X_{\mathrm{VPHCl}} > 0.5$, W_a/W_c rises rapidly to values >1.

The points above indicate that for many feed mixtures 1 : 1 stoichiometry is not observed. A general trend for both orders of addition is evident; i.e. when X_{VPHCl} is low, W_a/W_c is low, and as X_{VPHCl} increases, W_a/W_c tends to increase accordingly. In our study of PEC from mixing P2VP and PAMPS in ethanol/water, we reported[9] that W_a was greater than W_c for four out of five feed mixtures examined. Moreover, four from five precipitates analysed showed the mole fraction of AMPS$^-$ units present in the PEC to be nearly constant with a value between 0.50–0.55.

The precipitate compositions and trends in W_a/W_c

Table 3 PEC compositions determined from u.v. analysis of supernatant liquids in series 2

X_{VPHCl} in feed	VPH^+ in washings ($\times 10^4$ mol)	VPH^+ in washings (g)	VPH^+ in feed (g)	VPH^+ in PEC (g)	W_a of PEC (g)	VPH^+ in PEC ($\times 10^4$ mol)	X_{VPH^+} PEC (± 0.01)
0.100	0.41	0.0044	0.0639	0.0595	0.0722	5.59	0.90
0.200	1.20	0.0128	0.1278	0.1150	0.1647	10.8	0.82
0.300	3.50	0.0373	0.1917	0.1544	0.2637	14.5	0.73
0.400	2.30	0.0245	0.0852	0.0607	0.1251	5.70	0.65
0.500	2.80	0.0298	0.1065	0.0767	0.1464	7.20	0.68
0.600	1.20	0.0128	0.1278	0.1150	0.2342	10.8	0.65
0.700	3.90	0.0415	0.4473	0.4058	0.8808	38.1	0.66
0.800	20.4	0.2173	0.5112	0.2939	0.4877	27.6	0.75

Table 4 Molalities of salt required to suppress PEC formation for total polymer concentrations of (a) 12.3 g dm^{-3} and (b) 1.23 g dm^{-3}

Salt	Molality (a)	Molality (b)
NaCl	1.70	1.57
NaBr	1.73	1.59
LiBr	1.67	1.50

obtained from mixing the free acid and free base contradict those reported here. We maintain, however, that departures from 1 : 1 stoichiometry are probably due in the first instance to the existence of unreacted moieties in the PEC. We do not expect perfect pairing of sulfonate and pyridinium ions, and those unpaired will be accompanied by their corresponding counterions. The presence of counterions in the complex affects the calculation of PEC composition via elemental analysis by lowering the weight percentage of sulfur present in the complex and hence the mole fraction of $AMPS^-$ units in the complex.

In the system studied here, PEC formed from the addition of PAMPSNa to PVPHCl contain an excess of vinylpyridinium (VPH^+) groups which is far greater than the experimental error limits for 1 : 1 stoichiometry outlined by Philipp *et al.*[11]. An excess of cationic groups in PEC has also been noted by Fuoss and Sadek[10] in their pioneering study on PEC from mixing dilute aqueous solutions of poly(vinylbutylpyridinium bromide) and poly[sodium(styrenesulfonate)]. A possible explanation for this apparent excess of polycation in the PEC may be found by considering the basic strength of the pyridine group in the PVP homopolymer. It is reported elsewhere[16,17] that: (1) the pK_a of P4VP in water is 4.2 at 298 K; (2) the complete protonation of P4VP by strong acids is difficult to achieve. Consequently, fully ionized aqueous solutions of PVPHCl have pH values considerably less than 7. A 0.1 M solution of PVPHCl has an observed pH of ~2. Mixing solutions of 0.1 M PVPHCl and 0.1 M PAMPSNa (pH ~7.0) yields solutions having pH values intermediate to those quoted above. It is apparent therefore that the pH of individual reaction mixtures affects the ratio of protonated to unprotonated groups along the polymer chain. As pH rises above 2.0, the ratio of protonated groups to unprotonated groups decreases rapidly. The unprotonated groups cannot form ionic crosslinks with sulfonate moieties and, in order to retain electrical neutrality, unreacted $AMPS^-$ groups in the PEC remain bound to sodium counterions.

U.v. analysis

PEC compositions determined from u.v. analysis of supernatant liquids in series 2 are presented in *Table 3*. Each PEC composition was obtained from the concentration of unreacted VPH^+ detected in the supernatant liquid as follows:

1. the weight of VPH^+ units in the supernatant liquid was subtracted from the weight in the feed mixture to yield the weight of VPH^+ present in the complex;
2. this weight was subtracted from W_a to provide the mass of $AMPS^-$ units present in the precipitate, allowing the mole fraction of VPH^+ (X_{VPH^+}) in PEC to be determined.

An estimate of experimental error of ±0.01 has been appended to the mole fractions of each precursor in PEC shown in *Table 3*. Although there may have been errors in transference losses, the only way of making a quantitative estimate is to invoke the standard deviation in the calibration, i.e. determination of molar extinction coefficient of PVPHCl. PEC compositions calculated from u.v. data are in good agreement with elemental analysis results. U.v. analysis results for series 1 do not agree with elemental analysis results, as the data are unreliable due to long-term storage of supernatant solutions prior to u.v. analysis.

Suppression of PEC formation using salts

The limiting salt concentrations required to suppress PEC formation are listed in *Table 4*, which shows that prevention of PEC formation is not affected significantly by either the nature of the salt or the total concentration of polymer. Furthermore, it was discovered that changing feed mixture compositions X_{VPHCl} in the range 0.2–0.8 did not affect individual salt concentrations profoundly. An attempt to suppress PEC formation was made using the following salts in addition to those already mentioned: lithium fluoride (LiF), sodium thiocyanate (NaSCN), sodium perchlorate ($NaClO_4$) and sodium tetraphenylborate ($NaB(Ph)_4$). Qualitative tests showed that precipitation occurs upon mixing dilute aqueous solutions of PVPHCl with solutions of the first three salts. The pH of LiF solutions was too high to allow PVPHCl to remain in solution when mixed. In the case of aqueous NaSCN, a reaction occurred upon mixing that turned the solution yellow and caused the precipitation and colouration of the polymer. Precipitation occurred also when solutions of PAMPSNa and $NaClO_4$ were mixed; the interpretation of feasible reactions occurring as these solutions are mixed is beyond the scope of this paper, but a preliminary search of the literature suggested that PVPHCl may act as a chain transfer catalyst in a reaction where NaSCN undergoes nucleophilic substitution to form trithiocyanic acid[18]. It was found that $NaB(Ph)_4$ solutions of sufficient concentration to suppress PEC formation could not be made at 298 K.

D.s.c. and n.m.r. measurements

By means of d.s.c., values of 426 and 386 K were obtained for the glass transition temperatures of PVPHCl and PAMPSNa, respectively. These values lie in reasonable accord with the corresponding ones yielded by n.m.r., i.e. 412 and 394 K, respectively. By neither technique was it possible to obtain a T_g for the PEC, which is presumably a consequence of the very high density of ionic crosslinks present[19]. For all precipitates, broad melting peaks were recorded at $\sim$470 K and decomposition of samples occurred above 520 K.

CONCLUSIONS

This study has shown that PEC formed by mixing PAMPSNa and PVPHCl in water are non-stoichiometric and that the composition of precipitates is dependent upon order of addition. In previous related work[8,9], it was noted that departures from 1 : 1 stoichiometry occurred for certain feed mixtures, but that order of addition did not affect PEC composition. It was proposed that deviations are possibly caused by inactivation of ionic groups due to protonation or deprotonation of anionic and cationic groups, respectively. For the present system, the same rationale is presented. To date, we have reported data with respect to PEC reaction stoichiometry obtained after the isolation of precipitates. In order to explain the reasons for deviations from 1 : 1 stoichiometry described here, and the effect of order of addition on reaction stoichiometry, we are currently using conductometric, potentiometric and turbidimetric techniques *in situ* during PEC formation.

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