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Isothermal titration calorimetric studies of the acid–base properties of poly(*N*-isopropylacrylamide-co-4-vinylpyridine) cationic polyelectrolyte colloidal microgels

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Abstract

Isothermal titration calorimetry (ITC) and potentiometric titration were used to study the protonation properties of the 4-vinylpyridine (4-VP) moiety in cationic poly(*N*-isopropylacrylamide-co-4-vinylpyridine) colloidal microgels [poly(NIPAM-co-4-VP)]. Calorimetric pH titrations were performed using microgels of different 4-VP content and the influence of ionic strength and counter ions have been examined. The calorimetric titration output consists of several thermal contributions reflecting the complex nature of the interactions in the aqueous microgel dispersions. In contrast to the potentiometric results, the calorimetric titration data could not be completely described by a theoretical model solely taking into account protonation equilibria. Deviations from the proposed model correlate with swelling or shrinking of the gel particles. The calorimetric results also reveal a pronounced counter-ion effect of perchlorate compared to chloride ions. In the presence of perchlorate ions, small secondary thermal effects accompany protonation of the 4-VP moiety due, in part, to kinetically limited conformational changes in the co-polymer microgel.

Keywords: Isothermal titration calorimetry; Potentiometric titration; Protonation; Cationic colloidal microgel; 4-Vinylpyridine; Co-polymer

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1. Introduction

Cross-linked poly(*N*-isopropylacrylamide) [i.e. poly (NIPAM)] microgels have attracted significant interest in the recent scientific literature [1–11] due, in part, to their interesting physico-chemical properties; in particular, the ability to undergo reversible volume phase transitions (VPTs) in aqueous dispersions. The VPT properties can be amplified and controlled by co-polymerization with monomers constituted of ionisable functional groups [12]. Consequently the physico-chemical properties of colloidal microgels based on poly(NIPAM) and various co-polymer derivatives, have been widely investigated [1,2,4,11] in relation to the VPT changes that occur in response to a number of external stimuli such as pH [13], temperature [1,3] and ionic strength [13,14].

As a result of their diverse VPT properties in different dispersion environments, such microgels offer opportunities for use in a wide range of applications. Examples include water purification [15,16], controlled release of drugs [4,17], rheology modification [18] and opto-electric switches [19,20]. A number of techniques have been extensively used to characterize these gels, including photon correlation spectroscopy (PCS) [13], transmission electron microscopy (TEM) [21], differential scanning calorimetry (DSC) [13,22], isothermal titration calorimetry (ITC) [23–25], rheology [26] and nuclear magnetic resonance spectroscopy [27].

Surprisingly, perhaps, the scientific literature is not replete with reports of ITC studies of synthetic organic polymeric systems. Examples do, however, include the use of ITC (employing a thermal activity monitor calorimeter instrument) for investigations of the thermodynamics of molecular recognition reactions of non-covalently imprinted polymers [28]. In addition, the aggregation

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behavior of “mono-endcapped hydrophobically modified poly(sodium acrylate)s” [29] and the dissolution behavior of hydrophobically modified alkali-soluble polymer emulsions [24] in aqueous solution have also been analyzed by ITC techniques. Other studies employing ITC, carried out recently, have examined the interactions between poly(*N*-isopropylacrylamide) microgels and amino acids [30] as well as sodium dodecyl sulfate (SDS) [23]. Such measurements provide information on the thermodynamic parameters associated with the interactions between polymer systems in solution and other solvents.

Recently, a variety of physico-chemical properties of cationic poly(*N*-isopropylacrylamide-co-4-vinylpyridine) [poly(NIPAM-co-4-VP)] colloidal microgels were reported by Pinkrah et al [31]. The swelling behavior of these gels is strongly affected by the 4-VP content, the degree of protonation of the ionisable groups (which is, of course, controlled by the pH) as well as ionic strength and counter-ion effects—all of which, obviously, imply an underlying complexity in relation to the interactions taking place. Using potentiometric titrations, it was possible to calculate the number of protonatable sites and the characteristic pK_a values.

The objective of the current contribution is to complement the potentiometric results with calorimetric pH titration experiments providing additional information on the energetics of the interactions. The measurements have been carried out at two fixed ionic strengths (0.01 and 0.1 mol dm^{-3}) using co-polymer microgels incorporating different percentages of 4-VP.

2. Experimental

2.1. Materials

All chemicals (Aldrich, UK) were of analytical quality and used without further purification.

2.2. Microgel preparation

Poly(NIPAM-co-4-VP) microgel particles synthesized using different percentages of 4-VP (15, 25, 35, 45 and 55%) in the initial reaction mixture were prepared by surfactant-free emulsion polymerization and purified and characterized as described previously [31]. The reaction takes place in a single container by combining the monomer, cross-linker and initiator under a nitrogen atmosphere for 6 h with continuos stirring. The final concentration of the aqueous colloidal microgel stock dispersions was 0.52% (w/w).

2.3. Isothermal titration calorimetry (ITC)

All titration calorimetric measurements were carried out on a MCS titration calorimeter (MicroCal Inc., Northampton, MA) at 25 °C. Freshly distilled deionized water was used for preparing all solutions. Microgel dispersions of 0.05% (w/w) were prepared by dilution of the stock dispersions and adding appropriate amounts of $NaClO_4$ or NaCl to adjust the ionic strength (*I*) to 0.01 and 0.1 mol dm^{-3}, respectively. All solutions and colloidal samples were degassed prior to ITC experiments. The reference cell was filled with deionized water. The microgel dispersions were filled into the sample cell of the calorimeter ($v_{\text{cell}} = 1.3098\ \text{cm}^3$) and titrated with 0.01 mol dm^{-3} $HClO_4$ or HCl, also adjusted to a constant ionic strength of either 0.01 mol dm^{-3} or 0.1 mol dm^{-3}. All solutions were identical to those used for the potentiometric experiments. The acid was added in portions of 10 μl from a computer controlled syringe acting as a stirrer by rotating at 400 rpm, to ensure thorough mixing of reaction components. Titration experiments consisted of 25–30 injections (the duration of each injection was 25 s) with an appropriate time delay (300–3600 s) between the injections, allowing the reaction mixtures to equilibrate. The variable time delay reflects a change in the reaction rate as the reaction proceeds which in turn requires a longer period of time for the equilibrium to be achieved. Raw data were obtained as a plot of heat flow (μW) against time (h). The heat associated with each injection was calculated by integration of the peaks in the heat flow curve using the instrument software (ORIGIN®) provided by the instrument manufacturer. The calibration of the instrument was checked by dilution of an aqueous propan-1-ol solution (10 wt.%) into water [32].

Experiments were performed at the two different ionic strengths for each set of microgel dispersion studied, except for microgels with 45 and 55% 4-VP content at 0.1 mol dm^{-3} ionic strength. These dispersions started to coagulate after ca. 2 h and were not stable in the calorimeter during the measurement time. Blank experiments were performed under identical experimental conditions by titrating the acids into the corresponding pure electrolyte solutions of the same ionic strength. The blank effects were subtracted in order to correct for dilution, mixing and injection effects.

2.4. Potentiometric titrations

Potentiometric titrations were performed at 25 °C using a digital pH-meter (model 7065, Scientific Instruments Limited, UK) and a pH-electrode (model 1058 Scientific Laboratory Supplies, UK). The pH-electrode was calibrated against standard buffer solutions of pH = 3, 7 and 10 (Aldrich Hydrion Buffers) before each titration. Freshly distilled water was used for preparing all solutions. Microgel dispersions of 0.05% (w/w) for pH titrations were prepared by dilution of stock dispersions and adding appropriate amounts of $NaClO_4$ to adjust the ionic strength to 0.01 and 0.1 mol dm^{-3}, respectively. Dispersions of 13.1 cm^{-3} were titrated with 0.01 mol dm^{-3} $HClO_4$ in steps of 50 μl to a final pH <3 in order to achieve full protonation of the available pyridine sites. The pH values were recorded after an equilibration period of at least 2 m. The 0.01 mol dm^{-3}

$HClO_4$ titrant was standardized by using a 0.01 mol dm^{-3} NaOH solution. The perchlorate anion was used as a counter ion to control ionic strength because of its low ability to form complexes or ion pairs.

3. Results and discussion

Prior to presentation of the results and discussion the following points should be noted. It is important to appreciate, as stated above, that the physico-chemical characterization of the poly(NIPAM-co-4-VP) microgels investigated have been presented elsewhere [31]. Secondly, the exact 4-VP/NIPAM ratio within each co-polymer, relative to the composition of the feed monomers is not certain. A semi-quantitative spectrophotometric analysis of the different co-polymer microgels does, however, reveal a correlation between the concentration of 4-VP in the monomer feed and the level of 4-VP in the resulting colloidal particles [31]. More comprehensive studies of the detailed composition and structure of the co-polymer microgels are complex and non-trivial. Detailed studies of the structure, morphology and degree of cross-linking of the co-polymer microgels are currently the subject of long-term investigations in our laboratories. Finally, it is to be emphasized that all the calorimetric and potentiometric results were reproducible (a minimum of three replicates were carried out for each sample measured) and repeatable using multiple synthesis of different batches of the various co-polymer microgels.

Experimental results of calorimetric and potentiometric pH titrations at two different ionic strength values and with perchlorate as the counter ion for the co-polymer microgels are summarized in Fig. 1.

The observed enthalpies of interaction per mole of acid injected are exothermic and decrease with the extent of reaction. However, the shapes of the calorimetric titration curves are far from being simple—expressing the complex nature of the underlying process. As the percentage of 4-VP in the polymer matrix increases, the number of protonatable sites also increases and, hence, the consumption of acid (Fig. 1). There is also an effect of ionic strength. The potentiometric results show an increase in the concentration of available protonatable sites and a reduction in acidity (increase of pK_a) with increasing ionic strength due to charge screening and conformational changes induced by higher electrolyte concentration. In the calorimetric results decreased exothermic effects at the beginning of the titration and slightly larger enthalpies towards the end of the titration are observed as a function of ionic strength. The potentiometric titration curves can be described by means of a thermodynamic-based model using a minimum of two simultaneous protonation equilibria (two pK_a values or $n = 2$ in Eq. (1); see also Fig. 1). This can be understood by taking into account the polyelectrolyte effect in a polymer containing one type of protonable group (4-VP). The potentiometric model is based on

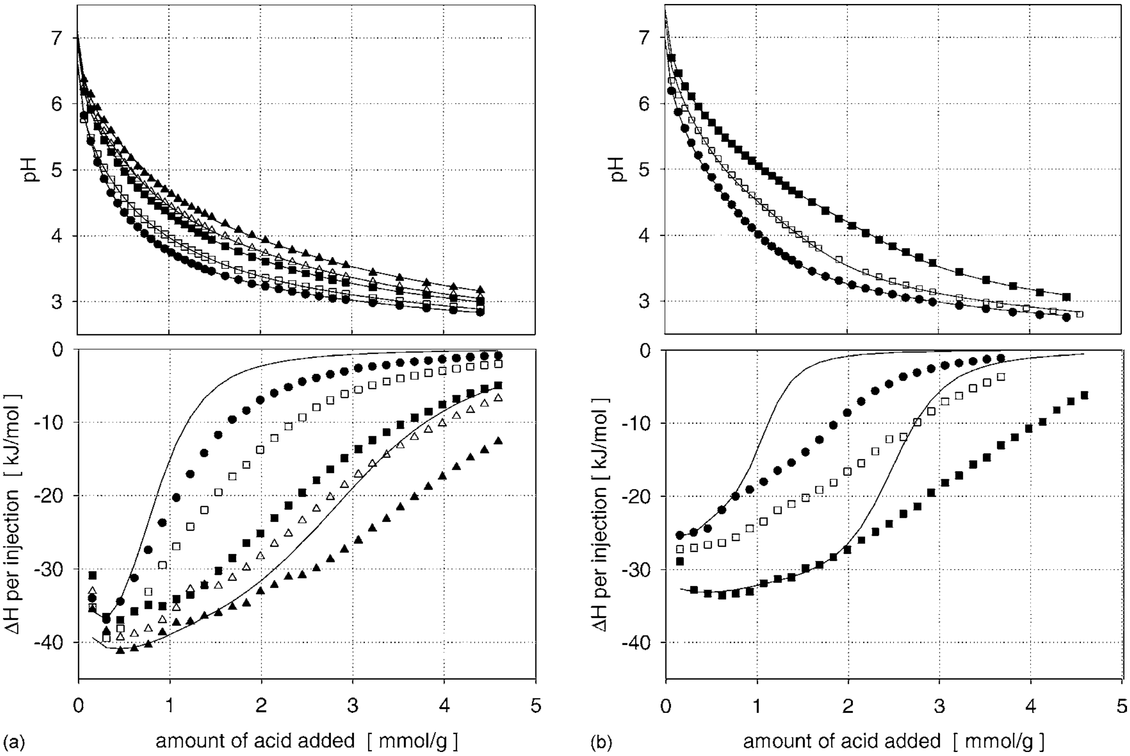

Fig. 1. Experimental (symbols) and calculated (lines) potentiometric and calorimetric pH titration curves at (a) $I = 0.01$ mol dm^{-3} and (b) $I = 0.1$ mol dm^{-3} adjusted with $NaClO_4$. (●) 15%, (□) 25%, (■) 35%, (△) 45% and (▲) 55% 4-VP.

the charge balance equation for the dispersion [33,34]:

$$C_{\mathrm{H^+}} - C_{\mathrm{OH^-}} + \sum_{1}^{n} \left(C^0_{\mathrm{HB}_i{}^+} \frac{10^{\mathrm{p}K_{\mathrm{a}_i} - \mathrm{p}K_\mathrm{W}}}{10^{\mathrm{p}K_{\mathrm{a}_i} - \mathrm{p}K_\mathrm{W}} + 10^{\mathrm{pH} - \mathrm{p}K_\mathrm{W}}} \right) - C_{\mathrm{acid}} = 0 \qquad (1)$$

where

$$C_{\mathrm{H^+}}\ (\mathrm{mol\,dm^{-3}}) = \frac{10^{-\mathrm{pH}}}{\gamma_{\mathrm{H^+}}} \quad \text{and}$$

$$C_{\mathrm{OH^-}}\ (\mathrm{mol\,dm^{-3}}) = \frac{10^{\mathrm{pH}-\mathrm{p}K_\mathrm{W}}}{\gamma_{\mathrm{OH^-}}}$$

In Eq. (1) $\gamma_{\mathrm{H^+}}$ and $\gamma_{\mathrm{OH^-}}$ denote the activity coefficients of hydrogen and hydroxide ions, K_W the dissociation constant of water, K_{a_i} the acid constant of the ith site, the total concentration of protonable sites, i, in mol dm^{-3} and the concentration (mol dm^{-3}) of acid titrated into the colloidal dispersion.

By fitting Eq. (1) to the potentiometric data with n = 2 the characteristic pK_a values and the total concentrations of the available protonable sites can be estimated (see Table 2 in [31]). In addition, Eq. (1) also provides the means to calculate the apparent concentration of all species in the dispersion enabling the extension of this approach towards the approximation of calorimetric titration curves [35]. Taking into account only acid–base equilibria, the exothermic heat (Q) during titration of the microgel with an acid arises from neutralization of the hydroxyl ions:

$$\mathrm{OH^-} + \mathrm{H^+} \xrightarrow{\Delta} \mathrm{H_2O}, \quad Q_\mathrm{N} = \Delta_\mathrm{N} H\, \Delta n(\mathrm{OH^-}) \qquad (2)$$

and from the dissociation of the basic sites B$_i$ (4-VP):

$$\mathrm{B}_i + \mathrm{H_2O} \xrightarrow{\Delta} \mathrm{HB_i{}^+} + \mathrm{OH^-}, \quad Q_{\mathrm{D}i} = \Delta_\mathrm{D} H_i\, \Delta n(\mathrm{HB_i{}^+}) \qquad (3)$$

In Eqs. (2) and (3) $\Delta_\mathrm{N} H$ denotes the molar enthalpy of neutralization ($\Delta_\mathrm{N} H = -55.8$ kJ mol^{-1} at 298 K [36]), $\Delta_\mathrm{D} H_i$ the molar enthalpy of dissociation of site i (adjustable parameter) and Δn the number of moles of acid reacted which can be calculated from the concentrations of the species and the volume of the dispersion. The total heat (Q_T) is the sum of all contributions:

$$Q_\mathrm{T} = Q_\mathrm{N} + Q_{\mathrm{D}i} \qquad (4)$$

The enthalpy of protonation of site i, $\Delta_\mathrm{P} H_i$, is obtained from Eqs. (2) and (3):

$$\Delta_\mathrm{P} H_i = \Delta_\mathrm{N} H + \Delta_\mathrm{D} H_i \qquad (5)$$

The results of applying this approach, considering the parameters from the fit of the potentiometric data (pK_{a_i} and concentrations), are shown in Fig. 1 as solid lines and summarized in Table 1. For clarity only two typical calculated curves are shown in each figure.

In contrast to the potentiometric titration curves a theoretical description of the calorimetric titration data, based on protonation reactions, proved difficult. In all cases only the first part of the calorimetric titration curve, corresponding to a pH of ca. 4, could be approximated satisfactorily. Below this pH, the experimental data show a large deviation indicating additional exothermic contributions that may be attributed to the swelling of the gel particles accompanied by conformational changes and increasing solvent interactions (hydration). This result is fully compatible with PCS investigations [31] showing a sharp increase in the hydrodynamic diameter of the co-polymer microgels over the pH interval from 4 to 3. The measured and calculated interaction enthalpies of the microgels are also different to the protonation enthalpy of pure 4-VP that has been determined to be −25.4 kJ mol^{-1} and independent of ionic strength. Hence, the interaction enthalpies of the microgels are sensitive to the 4-VP content and to the ionic strength suggesting a high degree of cooperativity in the collapsed state of the gels. In contrast to the microgels, the calorimetric titration curves for 4-VP could be described by the protonation model.

Table 1
Calculated enthalpies of protonation for poly(NIPAM)-co-4-VP microgels at different ionic strengths (25 °C)

	$\Delta_\mathrm{P} H_1$ (kJ mol^{-1})	$\Delta_\mathrm{P} H_2$ (kJ mol^{-1})
$I = 0.01$ mol dm^{-3}		
4-VP	−25.4	–
15% Poly(NIPAM)-co-4-VP	−36.0	−52.8
25% Poly(NIPAM)-co-4-VP	−40.2	−51.9
35% Poly(NIPAM)-co-4-VP	−38.1	−45.2
45% Poly(NIPAM)-co-4-VP	−39.8	−43.0
55% Poly(NIPAM)-co-4-VP	−41.9	−43.9
$I = 0.1$ mol dm^{-3}		
4-VP	−25.4	–
15% Poly(NIPAM)-co-4-VP	−28.0	−24.1
25% Poly(NIPAM)-co-4-VP	−27.9	−27.4
35% Poly(NIPAM)-co-4-VP	−34.2	−33.0

A detailed inspection of the raw calorimetric titration data reveals an interesting kinetic effect, as shown in Fig. 2. At an ionic strength of 0.1 mol dm^{-3}, adjusted with NaClO$_4$, the calorimetric signals are characterized by a slow enthalpic event following a larger and faster event. The signal needs about 50 min to completely return to the baseline. At a lower ionic strength, of 0.01 mol dm^{-3}, a similar behavior could only be observed during the initial injections with microgels containing more than 25% 4-VP. The slow heat effect disappears when a pH of ca. 4 is reached and the swelling of the microgel (VPT) starts. Therefore, the slow process appears to be related to the size of the microgel particles. It is known that increasing the percentage of 4-VP in the co-polymer microgel, pH values above 4 or increasing ionic strength all cause a decrease in the hydrodynamic diameter of the particles resulting in a shrunken, compact microgel structure [31]. Protonation reactions in such a compact, macromolecular structure should be accompanied by time-dependent processes such as conformational changes. It is worth mentioning that a similar effect could not be detected in the

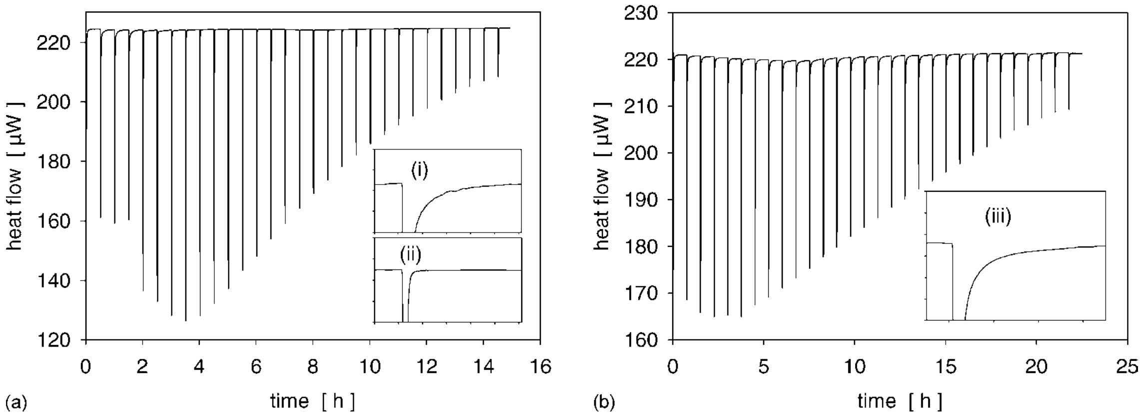

Fig. 2. ITC data for poly(NIPAM)-co-4-VP (35% 4-VP) titrated with perchloric acid at (a) $I = 0.01\,\text{mol}\,\text{dm}^{-3}$ and (b) $I = 0.1\,\text{mol}\,\text{dm}^{-3}$ adjusted with $NaClO_4$; zoomed parts show representative peak shapes, (i) peak 3, (ii) peak 10, (iii) peak 10, in a 40-min (a) and 50-min (b) window, respectively.

potentiometric experiments. A more detailed analysis of the appropriate calorimetric data showed that the slow heat effect can be described in all cases by a first-order kinetic equation with a characteristic rate constant of $1/(300 \pm 20)\,\text{s}^{-1}$.

Pinkrah et al. [31] also pointed out that there is a significant effect of the counter ion on the hydrodynamic diameter of poly(NIPAM)-co-4-VP microgels, especially at lower pH values. The perchlorate anion showed a more pronounced effect than the chloride ion at the same ionic strength resulting in smaller gel particle sizes. Characteristic ITC results are summarized in Fig. 3.

The calorimetric results also indicate a significant effect of the counter anion. In contrast to the size measurements, the counter-ion effect is present over the pH range covered by the titration. The impact of the chloride anion appears to be much smaller than that of the perchlorate anion indicated by the fact that calorimetric results at $0.1\,\text{mol}\,\text{dm}^{-3}$ ionic strength, adjusted with NaCl, are comparable with the results at an ionic strength of $0.01\,\text{mol}\,\text{dm}^{-3}$ maintained with $NaClO_4$. In addition, no slow reaction event could be observed in the calorimetric signals when chloride ions were present even at high ionic strength or percentage 4-VP content. These calorimetric results generally confirm the trend already found by hydrodynamic diameter measurements [31]. However, the strong effect of the perchlorate ion is still not clearly understood.

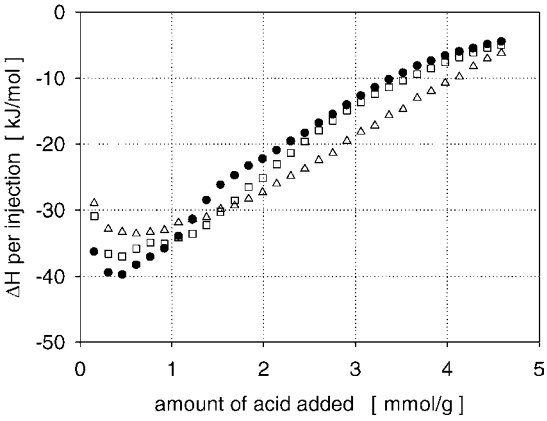

Fig. 3. Counter-ion effects on calorimetric titration results of poly(NIPAM)-co-4-VP 35%. (●) $I = 0.1\,\text{mol}\,\text{dm}^{-3}$ NaCl, (□) $I = 0.01\,\text{mol}\,\text{dm}^{-3}$ $NaClO_4$, (Δ) $I = 0.1\,\text{mol}\,\text{dm}^{-3}$ $NaClO_4$.

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