Journal of Colloid and Interface Science 370 (2012) 67–72

Contents lists available at SciVerse ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

pH induced swelling of PVP microgel particles – A first order phase transition?

Joseph Patrick Cook, David Jason Riley *

Department of Materials, Imperial College, Exhibition Road, South Kensington, London SW7 2AZ, UK

ARTICLE INFO

Article history:
Received 28 October 2011
Accepted 22 December 2011
Available online 4 January 2012

Keywords:
Microgel
Poly(2-vinylpyridine)
Phase transition
Light scattering
pH

ABSTRACT

The pH-induced swelling of poly(2-vinylpyridine) microgel particles was studied using dynamic light scattering. The increase in particle diameter with decreasing pH was modeled using a well-established thermodynamic model for microgel swelling. The Maxwell construction was applied to extend the model and yield a prediction for a pH-responsive microgel across the entire pH range. The model predicts a first order phase transition for polymer–solvent combinations with a Flory interaction parameter, χ, greater than a critical value χ_c. The modified theory compared favorably to the dynamic light scattering data for the hydrodynamic diameter of microgel particles based on 2-vinylpyridine at different pH values. In particular, the swelling transition is both predicted theoretically and observed experimentally to occur at a pH lower than the pK_a of the polymer.

1. Introduction

Microgels are colloidal cross-linked polymer particles which reversibly swell and collapse in response to changes in solvent parameters, namely temperature, pH and ionic strength [1]. Such particles have been synthesised using a variety of monomers such as *N*-isopropylacrylamide [2], vinylpyridine [3–7] and methacrylic acid [8], most commonly with divinylbenzene as a cross-linker. The swelling response to various stimuli can be tailored to specific needs by careful choice of monomer and synthesis conditions. Interest in microgels continues to grow as they find applications in an increasing number of fields. A prevailing area of microgel research is controlled uptake and release, particularly the potential for use in drug delivery [9,10]. Other applications include optical switches [11], microsensors [12] and rheological control [13]. Composite microgels are also receiving a great deal of attention [14].

Since the early work of Tanaka on macroscopic gels [15], many papers have been written that contribute to developing models for predicting polyelectrolyte behavior both for macroscopic gels and microgels. The underlying thermodynamic foundation is well-established and is based upon Flory's theory [16]. As is to be expected, different models are appropriate for different systems. For the temperature-dependent expansion and contraction of poly(*N*-isopropylacrylamide) (PNIPAM) particles Wu et al. [17] obtained an exceptionally good fit to experiment using an empirical expression for the Flory polymer–solvent interaction parameter, χ, and a form of Flory–Rehner theory, semi-empirically modified by Hino and Prausnitz [18]. Recently, an extremely thorough model that focuses on inhomogeneities in the nanostructure of PNIPAM microgel particles with a small fraction of incorporated organic acid, such as methacrylic acid, was developed by Hoare and Pelton [19], it includes effects such as Manning condensation, chain length distribution and stiffness. pH controlled swelling, with increases in diameter of five times or greater, has been reported for microgels based on methacrylic acid and poly(2-vinylpyridine) (PVP). Microgels based on methacrylic acid swell in reasonable agreement with the extent of ionisation of the particles predicted from their measured pK_a, with no need for a detailed thermodynamic model [20,21].

This paper is concerned with a detailed study of the pH-induced swelling of poly(2-vinylpyridine) (PVP) microgel particles [22]. To explain the swelling of PVP microgel particles on decreasing the pH the simplest possible thermodynamic approach, Flory–Huggins theory, for the swelling of a charged gel is applied. One difficulty with this simple model is the presence of loops in the swelling plot which make it difficult to produce physically sound predictions under certain conditions. In this study these loops are dealt with by an equal area construction analogous to the Maxwell construction for the Van der Waals equation of state, and microgel swelling theory is extended to a full pH response for PVP microgel particles cross-linked with divinylbenzene. It is demonstrated that experimentally determined particle size vs pH curves can be fitted using the extended theory, with one variable parameter k_M.

2. Theory

2.1. Microgel swelling theory

Microgels can be simply treated by considering the osmotic pressure inside a single particle. This can be represented by three

---

* Corresponding author. Fax: +44 (0) 207 5946751.
E-mail address: Jason.Riley@imperial.ac.uk (D.J. Riley).

0021-9797/$ - see front matter © 2012 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcis.2011.12.064

principle components for an ionic gel and only two for a neutral gel [23–26]. These contributions, assuming the swelling is isotropic and the cross-links are evenly distributed, are given below for a particle of diameter d, volume V and volume fraction of polymer within the particle ϕ. The values of these variables for the fully collapsed particle are denoted d_0, V_0 and ϕ_0 respectively.

The *mixing component*, π_m, arises from the increase in entropy associated with mixing two different substances:

$$\pi_m = -\frac{k_B T}{v_1}[\ln(1-\phi)+\phi+\chi\phi^2] \tag{1}$$

where k_B is the Boltzmann constant, T is the absolute temperature, v_1 is the volume of a solvent molecule and χ is the Flory polymer–solvent interaction parameter.

The *elastic component*, π_e, arises from the restriction of cross-linking on swelling:

$$\pi_e = \frac{k_B T N_c}{V_0}\left[\frac{\phi}{2\phi_0}\left(\frac{\phi}{\phi_0}\right)^{1/3}\right] \tag{2}$$

where N_c is the effective number of polymer chains within a particle. The effective number of chains may be estimated for a polymer of monomer 'a' cross-linked with a small amount of monomer 'b' using the expression [27]

$$N_c = 2N_A\frac{V_0\rho_b}{M_a+\left(\frac{1}{x_a}-1\right)M_b} \tag{3}$$

where N_A is the Avogadro constant, M_a and x_a are the relative molecular mass and mole fraction of monomer 'a' and M_b and ρ_b are the relative molecular mass and density of monomer 'b'.

The mixing and elastic components, both derived from Flory theory [15], are sufficient to describe neutral gels. Ionic gels require a third, *ionic component*, π_i, to account for the charge on the polymer network. If it is assumed that the salt concentration is low and that the charge fixed on the polymer network, Q_p, is sufficiently small that Manning condensation [28] cannot take place, the counterions inside the particle can be envisaged as exerting an osmotic pressure analogous to that of an ideal gas [29]. Thus, if the number of counterions inside a particle is equal to the charge fixed on the particle to maintain electroneutrality, the ionic component is given by:

$$\pi_i V = k_B T Q_p \tag{4}$$

At equilibrium there is no net transfer of solvent or ions across the interface between the particle and the bulk solvent and so the osmotic pressure inside the particle is zero:

$$\pi_{total} = \pi_m + \pi_e + \pi_i = 0 \tag{5}$$

$$[\ln(1-\phi)+\phi+\chi\phi^2] + \frac{v_1 N_c}{V_0}\left[\left(\frac{\phi}{\phi_0}\right)^{1/3} - \frac{\phi}{2\phi_0}\right] - \frac{v_1 Q_p}{V} = 0 \tag{6}$$

Fig. 1 shows solutions to Eq. (6) as a swelling plot of particle size against particle charge for a range of values of χ. A defining feature is that when χ lies above a critical value, χ_c, the charge on a particle ceases to be a monotonically increasing function of its diameter and vice versa. Loops on the swelling plot, evident for $\chi > \chi_c$, represent a physically unstable scenario in which an increase in particle size is accompanied by a decrease in particle charge.

The value of χ_c depends most strongly on the cross-link density. For particles of d_0 = 132 nm, a cross-link density of 0.1 wt% gives χ_c = 0.588, increasing steadily to χ_c = 0.704 for 2 wt%. Cross-links serve to restrict swelling and so increasing the cross-link density increases the value of χ_c by extending the region where the particle is insensitive to increases in particle charge.

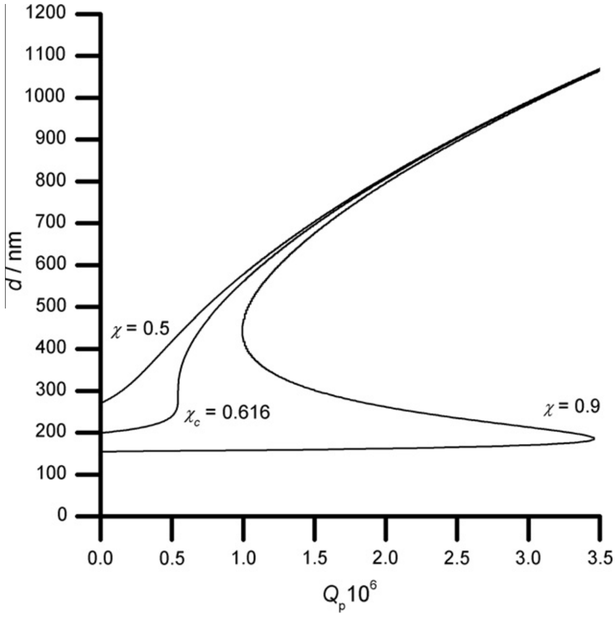

Fig. 1. Swelling plot of a microgel according to the Flory–Huggins thermodynamic model of Eq. (6). The parameters used were d_0 = 132 nm, cross-linker concentration = 0.5 wt% and ϕ_0 = 1. Q_p is the charge fixed on the polymer network and d is the particle diameter.

2.2. The Maxwell construction

Loops on the swelling plot bear a striking resemblance to Van der Waals loops, which result from the Van der Waals equation of state [30]. Similarities between microgel swelling theory and the Van der Waals equation of state should come as no surprise as they both fall into the universality class of mean field theory.

Van der Waals loops encompass regions of instability. A fluid system which increases in volume in response to an increase in pressure is, of course, unstable. Similarly, a microgel particle which contracts in response to an increase in network charge is unstable. Maxwell's solution to the problem of Van der Waals loops was to construct a tie line on the pressure–volume plot such that the areas between the loop and the tie-line are equal above and below the line [31]. This line encompasses the region of coexistence between a liquid and a gas in the case of a real fluid system and is constructed in this manner to ensure that the change in free energy on moving a system through the looped region is the same both with and without the tie-line modification. Since its original application, the Maxwell construction has found uses in modeling many diverse physical scenarios. Recent examples include hadron-quark phase transition in stars [32] and the adsorption of nitrogen molecules on the surface of fullerenes [33]. In order to apply the Maxwell construction to microgel swelling theory we re-plot the theory in the counter-intuitive manner of Fig. 2, with the volume per charge inside a particle (V/Q_p) being plotted against the particle charge (Q_p). An area on such a plot represents a volume. We construct our tie-line such that the areas between the loop and the tie-line are equal to the left and right of the line and thus the change in volume on moving through the looped region is equal both with and without the tie-line modification. Since the osmotic pressure is constant throughout, the work done is also equal.

The tie-line is constructed between volumes V_1 and V_2 where V_1 and V_2 satisfy the conditions

$$Q_p\ (V = V_1) = Q_p\ (V = V_2) \tag{7}$$