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Interfacial Tension and a Volume Phase Transition of Microgel Particles

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SUMMARY: A continuous volume phase transition of 2-vynilpyridyne microgel particles is described, both experimental and theoretically. The network charge was selected as the physical variable triggering the transition, which was followed by dynamic light scattering. The interpretation of the results with the Flory-Huggins thermodynamic model for gels suggests the consideration of effects leading to a new osmotic equilibrium. In previous works ion condensation was introduced to account for the unusual behaviour yielding interesting but not totally successful results. In the present paper, an alternative explanation based on an interfacial tension contribution to the total osmotic pressure is presented.

Introduction

A polymer gel is a three-dimensional crosslinked network immersed in a fluid, which is known to exhibit a macroscopic change in size whenever the interactions among their constituents or with the solvent molecules are modified. Because of their size within the colloidal range, microgels show interesting and novel properties, in which the nature of the gel plays an important role.

In this work we describe a continuous volume phase transition of 2-vynilpyridyne microgel particles. The network charge, controlled through the medium pH, was selected as the physical variable triggering the transition, which was monitored using dynamic light scattering.

The interpretation of the results was carried out with the Flory-Huggins thermodynamic model for gels. The encountered discrepancy between theory and experiment has been overcome by the consideration of new effects arising from the colloidal nature of the gel. Ion condensation was already considered in a previous work1), yielding a fairly good approach between theory and experiment, but leaving some discrepancies unsolved. In this paper we present a different explanation, based on an interfacial tension contribution to the swelling equilibrium. The physical

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insight of this new contribution will be given, as well as the improvements over the initial swelling theoretical curve.

Theory

Classical osmotic equilibrium

The total osmotic pressure inside an ionic gel consists of two terms related to the polymer network (mixing and elastic components), and a term due to the ion concentration difference inside and outside the gel (Donnan equilibrium)[2]. The mixing and elasticity osmotic pressures, π_m and π_e, respectively, are given by the following equations[3]:

$$\pi_m = -\frac{N_A k T}{v_s}\left[\phi + \ln(1-\phi) + \chi \phi^2\right] \qquad (1)$$

$$\pi_e = \frac{N_C k T}{V_o}\left[\left(\frac{\phi}{2\phi_o}\right) - \left(\frac{\phi}{\phi_o}\right)^{\frac{1}{3}}\right] \qquad (2)$$

The contribution due to the presence of the counter-ions may be expressed as[4]:

$$\pi_i = \frac{f\, N_C\, k\, T}{V_o}\,\frac{\phi}{\phi_o} \qquad (3)$$

The swelling is assumed to be isotropic and the number of chains appearing in equations (2) and (3) is estimated with the aid of the following equation[1,5]:

$$N_c = 2 N_A X = 2 N_A \frac{V_o\, \rho_{monomer}}{M_{crosslink} + \left(\frac{1}{x_{crosslink}} - 1\right) M_{monomer}} \qquad (4)$$

The equilibrium condition is expressed by equating to zero the total osmotic pressure:

$$\pi_{total} = \pi_m + \pi_e + \pi_i = 0 \qquad (5)$$

Ion condensation correction

The above theoretical model should be corrected for highly charged gels due to ion condensation$^{1)}$. The reduction of mobile counter-ions by condensation is simply modelled by considering an effective total number of mobile counter-ions $f^* = f\,(1 - g)$. Equation (3) may then be re-written as:

$$\pi_i^* = \frac{f\,(1-g)\,N_C\;k\,T}{V_o}\,\frac{\phi}{\phi_o} \qquad (6)$$

Interfacial tension contribution

The interfacial tension contribution of a macrogel/water interface has recently been used in order to describe the degree of swelling and the phase transition temperature of ionised N-isopropylacrilamide–co-acrylic acid gels$^{6)}$. This contribution has never been employed before in microgel/water interfaces. The idea rests on the thermodynamics of the polarizable interface$^{7)}$, stating that the presence of a surface charge density induces an interfacial tension. For a microgel, this interfacial tension should play a relevant role, since a great deal of charge is located at the surface due to the initiator employed in the synthesis.

These arguments lead to a modification of the total osmotic equilibrium due to the microgel interfacial tension. For a spherical particle, this new contribution can be written as:

$$\pi_s = -\frac{4\,\gamma}{d} \qquad (7)$$

and thus, equation (5) is replaced by:

$$\pi_{total} = \pi_m + \pi_e + \pi_i^* + \pi_s = 0 \qquad (8)$$

Experimental

The synthesis of the microgel particles employed throughout this work is described elsewhere[8)]. They are based on poly(2-vinylpyridine) (2VP), crosslinked with divinylbenzene. The initiator used was 2,2' – azobis(2-amidinopropane) dihydrochloride (V50, Wako).

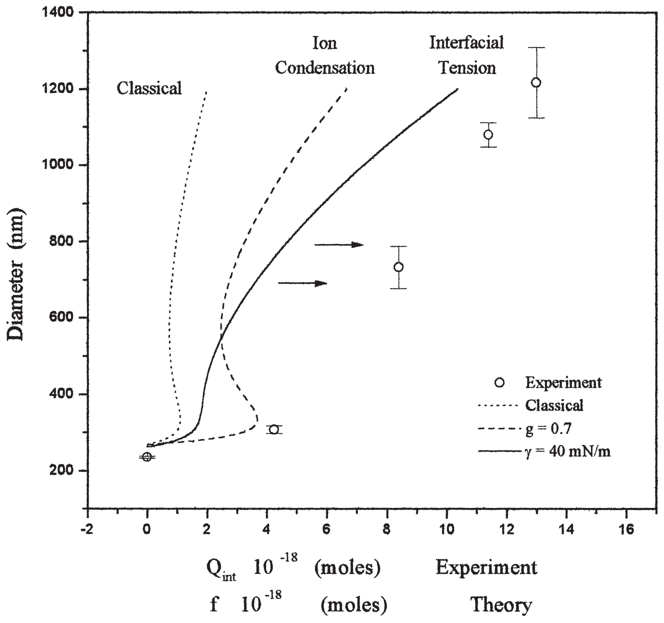
Transmission electron microscopy (TEM) showed the particles to be spherical and highly monodisperse, with a diameter of (205 ± 8) nm[8)]. This is considered to be the collapsed size, and hence, the polymer volume fraction associated will be 1.

The bulk charge per microgel particle (Q_{int}) was determined by both conductimetric and potentiometric titrations. The average hydrodynamic diameter was measured using dynamic light scattering. Dispersions were prepared at a concentration of $5\cdot 10^9$ particles cm^{-3}, adjusting the ionic content to 1 mM of Cl^- ions.

Results and Discussion

The phase transition is discussed in a size-charge diagram. The following figure shows the experimental relation between hydrodynamic diameter and bulk charge, together with several theoretical approaches. The experimental behaviour shows that: (a) until a certain bulk charge value is reached ($\approx 4\cdot 10^{-18}$ moles), the swelling is not very sensitive to the charge stage, (b) above this region, any further increase of Q_{int} causes a relevant increase in particle size, (c) in the absence of inner charge, the particle diameter is close to the TEM (collapsed state) value, and (d) the non-occurrence of a discontinuous phase transition.

The classical model does not describe the experiment for any value of the Flory interaction parameter. Moreover, a non-observed discontinuous phase transition is predicted. In the figure, the theoretical curve corresponding to $\chi = 0.7$ is plotted. As can be seen, only the first experimental point (collapsed state) coincides with the prediction.



Ion condensation was previously described for explaining the above differences[1], improving the description but leaving some unsolved discrepancies. This correction describes adequately the initial non-sensitivity zone (see figure). Moreover, the experimental slope of the swelling curve at high sizes is improved with respect to the classical model. However, the inclusion of ion condensation enhances the occurrence of a discontinuous volume phase transition.

On the other hand, the single introduction of the interfacial tension contribution, modifies the theoretical swelling prediction in two ways: (a) makes continuous, the initial discontinuous transition characterised by a certain value of the Flory parameter; and (b) by decreasing the slope of the swelling curve. These two modifications are induced since the interfacial tension tends to diminish the microgel volume by lowering its surface. An increase of the polymer-solvent interaction parameter is necessary for observing the discontinuous phase transition. Moreover, this size reduction due to this interfacial tension also implies that the mobile counter-ion concentration within the gel has to be increased for obtaining a certain swelling diameter. Thus the slope of the swelling curve at high sizes is decreased.

A theoretical curve for $\gamma = 40\ mN/m^2$ is presented in the figure. The experimentally observed initial non-sensitivity with the increase in bulk charge is described. Once the swelling becomes noticeable, the interfacial tension contribution yields the non-occurrence of a discontinuous phase transition, as observed experimentally, also leading to a swelling rate closer to the experimental one.

The interfacial tension contribution describes qualitatively better the experimental results since it does not predict a discontinuous phase transition, which is unavoidable with the ion condensation correction. Moreover, for a quantitative agreement one expects that the network fix charge should be greater than the mobile number of counter-ions (Donnan effect), since some of the OH^- ions that arise from the ionisation of the network 2VP groups will migrate to the solution. In this way, the interfacial tension theoretical curve should displace itself to the right, improving the agreement with the experimental data. Unfortunately, this effect cannot be incorporated since the equilibrium concentration of the salt ions are not known.

References

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List of symbols

N_A : Avogadro constant

k : Boltzmann constant

T : temperature

v_s : molar volume of the solvent

ϕ_0 : volume fraction of polymer in the microgel particle

V_o : volume of the microgel particle in the unswollen state

ϕ : volume fraction of polymer in the swollen gel

N_C : effective number of chains

χ : Flory polymer-solvent interaction parameter

f : total number of counter-ions per polymer chain in the gel

X : moles of crosslinks

$\rho_{monomer}$, $M_{crosslink}$, $M_{monomer}$, $x_{crosslink}$: density, molecular weight and mole fraction

g : fraction of condensed ions per particle

γ : interfacial tension

d : microgel particle diameter

Q_{int} : bulk charge per microgel particle