

## Microgels: Novel Colloidal Materials

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Microgels are novel colloidal gels widely used because of the swelling or de-swelling exhibited under specific external conditions. In this work, the swelling and de-swelling of microgel particles is experimentally described. The medium pH, salt concentration and osmotic stress, are the three variables with which the change of phase has been realised. All transitions are found to occur well above the critical point of the system. Additionally, the basic applications in which the given transition is employed are described.

*Keywords: Microgel, swelling, flory theory*

### Microgeles: Un Nuevo Material Coloidal

Los microgeles son geles coloidales que se emplean por el inflado y/o desinflado que manifiestan ante ciertas condiciones externas. En este trabajo, se describe experimentalmente el inflado y el desinflado de partículas de gel. El pH del medio, su concentración iónica y el esfuerzo osmótico externo son las variables externas que se emplean para provocar el cambio de fase en las partículas. Todas las transiciones ocurren por encima del punto crítico del sistema. Adicionalmente, se presentan algunas de las aplicaciones en donde se emplea la transición provocada por la variable externa concreta.

*Palabras clave: Microgel, inflado, teoría de Flory*

## 1. 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 solvent molecules are modified. Microgel particles are gels with dimensions in the colloidal range.

Because of their size and gel nature, microgels are currently the focus of considerable scientific research. The reasons for such interest rest on their ability to respond reversibly to external stimuli (temperature, pH, ionic concentration, external stress or nature of the solvent) and also, in certain cases, because of their biocompatibility. Moreover, for applications where the swelling transition is required to be rapid, gels with very small dimensions are needed.

In the present paper, the volume phase transition of a microgel is theoretically described and studied from an experimental point of view. The solution pH, its ionic concentration and the external osmotic pressure were the selected variables for triggering the transition. For the microgel employed in this work, all transitions were found to be "continuous", meaning that the change of phase occurs above the critical point of the system. As a consequence, that transition cannot be regarded as strict thermodynamic phase transition, but just as a change of phase from the collapsed to the swollen state, or viceversa.

## 2. THEORETICAL DESCRIPTION OF THE VOLUME PHASE TRANSITION

The total osmotic equilibrium inside an ionic gel consists, basically of three contributions: mixing ( $\pi_m$ ), elastic ( $\pi_e$ ) and ionic ( $\pi_i$ ) (1,2). Explicitly:

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

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

$$\pi_i = \frac{f N_C k T}{V_o} \frac{\phi}{\phi_o} \quad [3]$$

where  $N_A$  is the Avogadro number,  $N_C$  the number of chains,  $k$  the Boltzmann constant,  $T$  the absolute temperature,  $v_s$  the molar volume of the solvent,  $V_o$  and  $\phi_o$  the volume and polymer volume fraction of the gel in the totally collapsed state,  $\chi$  the Flory interaction parameter,  $\phi$  the polymer volume fraction for a given state and  $f$  the number of counterions per chain inside the gel.

The equilibrium condition is expressed by:

$$\pi_{total} = \pi_m + \pi_e + \pi_i = 0 \quad [4]$$

In order to gain some insight about the behaviour of a microgel system, the particle size has been plotted versus the number of gel counter-ions ( $n = f N_C$ ) in figure 1, for different  $\chi$  values. For no gel counter-ions,  $\pi_i = 0$ , the swelling is controlled by the interaction between the solvent and the polymer. As  $\chi$  increases, the solvent-polymer contacts are less favoured than the polymer-polymer contacts and the particle de-swells. For low  $\chi$  values, the size increases monotonously with the number of gel counter-ions, while for high values of  $\chi$  it shows different trends. In this latter region, the curve resembles a liquid-vapour like transition curve, indicating two co-existing particle sizes for a given value of  $n$ . Equation (4) has three roots, leading to three different situations: the corresponding to stable states (the two coexisting phases: swollen and deswollen), the metastable region and a zone associated with the unstable states. Therefore, figure 1 corresponds to a form of the phase diagram of an ionised gel. The critical point of the system is found to be above  $\chi = 0.5$  and below  $\chi = 0.6$ . Below this value the gel experiences a "continuous" change of phase, and thus no first order transition is observed.

## 2. EXPERIMENTAL

### 2.1. Experimental system

The synthesis of the microgel particles employed throughout this work is described elsewhere [3]. They are based on poly(2-vinylpyridine) (2VP), crosslinked with divinylbenzene (0.25% by weight). The initiator used was 2,2'-azobis (2-amidinopropane) dihydrochloride, which confers amidinium groups to the particle surface. Transmission electron microscopy showed the particles to be spherical and highly monodisperse, with a diameter of  $(205 \pm 8)$  nm (3).

### 2.2. Experimental details

The average hydrodynamic diameter of the microgel particles was determined using homodyne, laser dynamic light scattering (Malvern Instruments). Dispersions were prepared at a particle concentration of  $5 \cdot 10^9$  cm<sup>-3</sup>.

The solution pH and ionic content were varied by adding HCl or NaOH and NaCl, respectively. For the pH swelling, the counter-ion concentration was adjusted to 1 mM. Equivalently, the pH was held fix when the changing variable was the ionic concentration of the medium.

The external osmotic pressure was exerted using a dextran solution. The dextrans employed (C<sub>6</sub>H<sub>10</sub>O<sub>5</sub> form Fluka. Number average molar mass,  $M_n = 70000$  g/mol) have been extensively studied and characterised elsewhere (4).

## 3. RESULTS: MICROGEL CHANGE OF PHASE

In this section the particle swelling or de-swelling will be presented in terms of the three following external variables: solution pH (section 3.1), ionic concentration (section 3.2) and dextran concentration (section 3.3).

### 3.1. pH swelling

Crosslinked copolymer gels formed from weakly ionizable

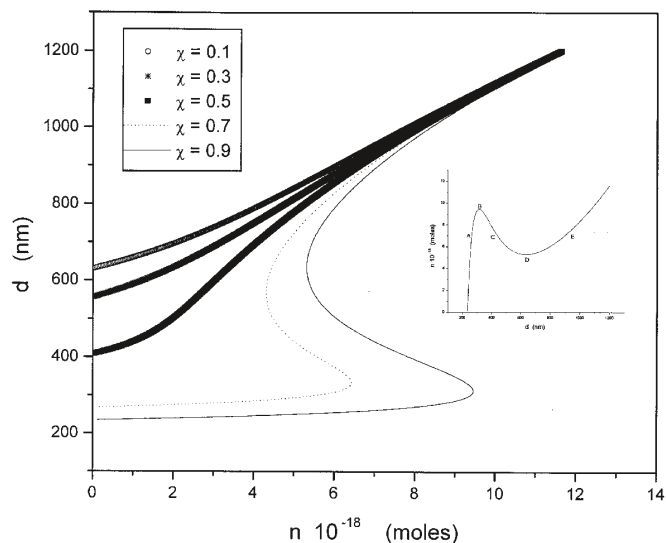


Figure 1: A form of a phase diagram of a gel according to Flory's thermodynamic theory.  $\chi$  is the Flory parameter controlling the transition. The critical point is found to be above  $\chi = 0.5$  and below  $\chi = 0.6$ .  $N_C = 204000$ . In the right hand side of the figure the curve for  $\chi = 0.9$  is plotted. The letters distinguish between stable (below A and above E), metastable (A-B and D-E) and unstable (B-D) regions.

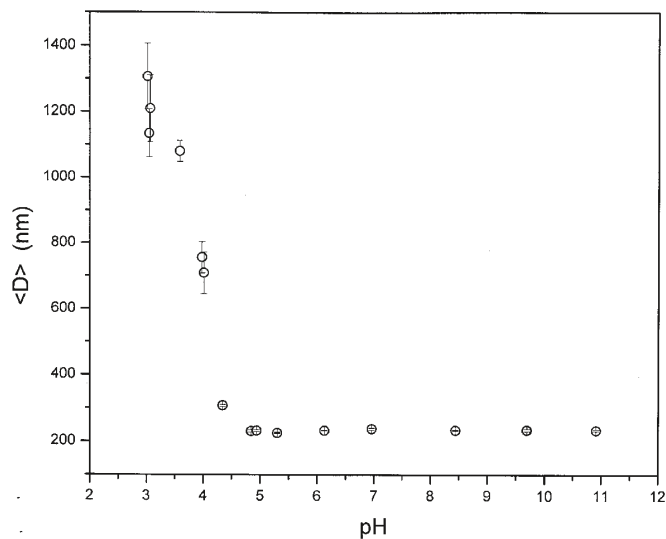


Figure 2: Hydrodynamic diameter versus pH. At pH 4.8 the size of the particles increases coinciding with the onset of the volume phase transition.  $[Cl^-] = 1$  mM.

monomers, exhibit pH-dependent swelling. The hydrodynamic diameter for the microgel particles is shown in figure 2 as a function of pH. As can be seen, the particle size is constant until the pH is lowered to pH 4.8. At this specific value, the microgel experiences a considerable increase in size, indicating the onset of the phase change from the collapsed to the swollen state. The swelling appears exactly when the 2VP groups ionise, indicating that the transition is controlled by the particle charge stage (5). The electrostatic interaction between the constituent monomers and the osmotic effect of the counter-ions, are what causes the particle change of phase.

The use of the charge controlled swelling of microgels is specially useful in drug delivery applications. The conditions of diffusional release of various bioactive agents is a subject to which plenty of attention has been paid (6). An additional

advantage of microgels (also of macrogels) is that they may provide desirable protection of drugs, peptides and specially proteins from the potentially harsh environment in the vicinity of the release site (7). Additionally, microgels may be excellent candidates as biorecognizable biomaterials, and thus could be used as targetable carriers of bioactive agents or bioadhesive systems (8).

The removal of heavy metal ions from aqueous systems with water purification purposes is another major application of colloidal gels (9). A major attraction of these systems for this specific application is their potential for regeneration after uptake of the contaminants. Furthermore, in comparison with macrogels, microgels have a large, effective surface providing rapid rates of adsorption, allowing high concentrations of contaminants to be removed rapidly.

Finally, we would like to stress that with the swelling, the particles index of refraction changes considerably approaching at the end that of the solvent. As a consequence, the solution opaqueness or transparency could be controlled. This fact enables the use of charged microgels as optoelectronic switches (10,11).

### 3.2. Ionic screening de-swelling

The fact that charged microgels swell basically due to electrostatic interactions, enables the possibility of causing a reduction of the interaction by screening their charge with the addition of ions to the solution. A Donnan equilibrium is established between the microgel and the surrounding medium, but as the counter-ion content in the solution rises the screening between charged monomers becomes increasingly more effective. Figure 3 shows the microgel hydrodynamic diameter versus the solution ionic concentration for a fixed pH. It is clearly seen how the particle de-swells as the salt concentration increases.

The salt effect on the swelling has interesting applications. As an example, it is useful to note that divalent  $\text{Ca}^{++}$  ions play an essential role in the contraction and relaxation of muscles, a process that in some respects seems to resemble the collapse of an ionised gel (11). The material itself as well as its salt dependent swelling, provide an excellent model of artificial muscle on the one hand and a certainly good way of gaining insight of any of the typical processes that take place in a real muscle.

### 3.3. Osmotic de-swelling

The effect of free polymer over the stability of colloidal systems has been widely studied. Depletion-flocculation phenomena has been introduced and extensively described (12). From another perspective, the effect of free polymer over a microgel system is presented in this section, in the polymer range over which no flocculation of the particles occurs. In this specific case, the particle reacts to the external osmotic stress by de-swelling (see figure 4). The dextrans contribute to the total osmotic equilibrium by exerting an additional osmotic pressure. The equilibrium condition expressed by equation 4 has to be modified in order to take this new contribution into account:

$$\pi_{total} = \pi_m + \pi_e + \pi_i + \pi_{dextran} = 0 \quad [5]$$

The consequence is an extraction of solvent from the particles, causing the observed de-swelling.

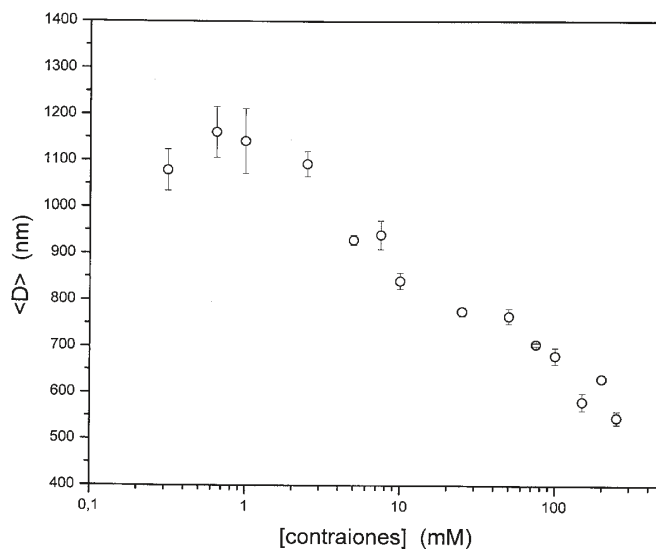


Figure 3: Hydrodynamic diameter versus salt concentration. pH 3.5.

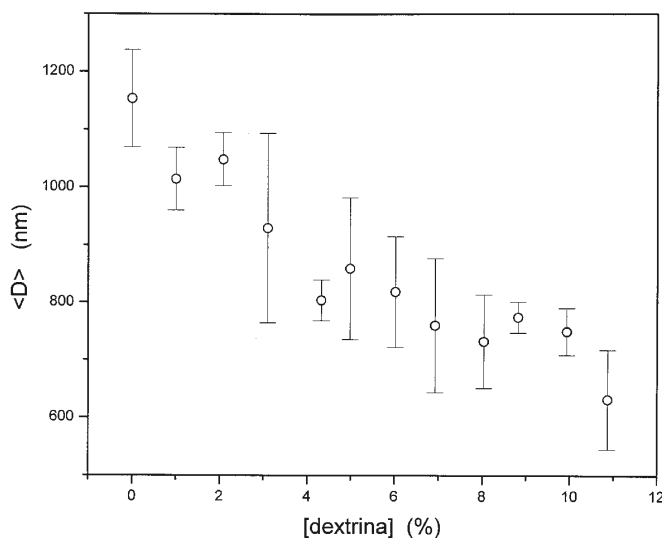


Figure 4: Hydrodynamic diameter versus dextran concentration. A given dextran concentration exerts a certain osmotic pressure that can be obtained as established in [4].  $[\text{Cl}^-] = 1 \text{ mM}$ . pH 3. The origin of the error bars, arise from experimental difficulties in measuring the diffusion coefficient for swollen microgels (index of refraction matching between colloid and solvent).

Microgels provide rheological control for high solids formulations employed in the surface coatings industry (13). The influence of added non-absorbing polymer on the swelling of microgel particles is of practical interest in this field and constitutes a major application of this type of studies (14).

## 4. SUMMARY

Charged microgels are novel colloidal materials offering a wide variety of possibilities from experimental and theoretical points of view, basically due to the union of the gel like properties as well as those arising from its colloidal nature. The "continuous" swelling of the particles induced by the network charge stage, its screening and the external osmotic stress has been presented here, emphasizing on the potential

applications of the observed behaviour. The modelization of the results is being carried out with the aid of Flory's thermodynamic theory for gels.

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