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Comparative thermodynamic study of functional polymeric latex particles with different morphologies

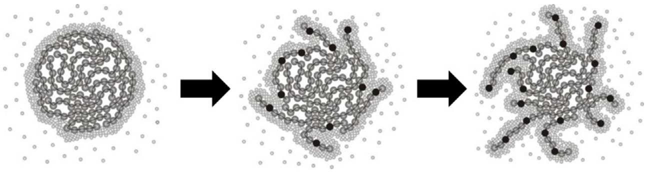
R. Santillán[a], E. Nieves[a], P. Alejandre[a], E. Pérez[a], J.M. del Río[b],**, M. Corea[a],*

[a] Instituto Politécnico Nacional, ESIQIE, UPALM, Edificio Z-6, Primer Piso, San Pedro Zacatenco, Del. Gustavo A. Madero, México, D.F., México
[b] Instituto Mexicano del Petróleo, Programa de Aseguramiento de la Producción, Eje Central Lázaro Cárdenas 152, Col. San Bartolo Atepehuacan, Del. Gustavo A. Madero, C.P. 07730 México, D.F., México

HIGHLIGHTS

- The swelling of a polymeric particle depends on hydration and free volume effects.
- Free volume depends on the composition and position of functional groups.
- Functional groups closer to the surface contribute more to conformational changes.
- The thermodynamic method shown helps the fine tuning of the polymeric material.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, the thermodynamic behavior of three series of functionalized polymeric particles with different morphologies and different functional group concentrations were compared. Partial volumes and partial adiabatic compressibilities of particles at infinite dilution were calculated from density and sound speed data. These properties were interpreted in terms of the atomic, free volume and hydration contributions. In addition, this interpretation was extended to the particle components (polar and non-polar groups), developing a new thermodynamic methodology. For homogeneous particles without forced gradient, functional groups are located from the surface to the interior and the voidness effect plays an important role in the swelling process. In multilayer particles, functional groups are located at the boundary of each layer and they are completely hydrated while non-polar groups behave as a permeable membrane at high functional groups concentrations. Homogeneous particles with forced gradient behave as homogeneous particles without forced gradient at low functional groups concentrations and as a multilayer particle at higher concentrations of functional groups. In conclusion the shown thermodynamic tool allowed understanding the role played by each particle component and its interactions inside the particle.

1. Introduction

Nano-sized materials have attracted substantial interest over several years due to their unique characteristics and versatility [1] which has enabled advances in polymer science. These advances have resulted in polymeric materials with unique properties [2]. Specifically, hydrogels have been received considerable attention [3] due to their stimuli–response capacity [4]. They can undergo abrupt volume changes in response to small changes in environmental [5] parameters, such as temperature [6,7], pH [8,9], ionic strength [10,11], electric field [12], light intensity [13] or the introduction of specific molecules [10,14].

Hydrogels are a three-dimensional, high molecular weight network; they can retain solvent at least 20% of their own weight. They

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* Corresponding author. Tel.: +52 55 57296000x54221.
** Corresponding author. Tel.: +52 55 91758203.
E-mail addresses: jmdelrio@imp.mx, jm.delrio.garcia@gmail.com (J.M. del Río), mcoreat@yahoo.com.mx, mcorea@ipn.mx (M. Corea).

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can swell significantly by absorbing water and shrink again after de-swelling [15–17]. In a swollen crosslinked or non-crosslinked hydrogel, the ionic groups inside polymer can facilitate the absorption of polar solvents or a reversible response an external stimulus [18–20]. The flexibility of polymeric chains allows the deformation need to accommodate solvent molecules in their interior. For non-crosslinked materials, the network has a physical origin (non-permanent) [21]. In other words, the polymeric chains are entangled with each other in a three-dimensional network retained the solvent and separated the chains for unlimited swelling by progressive solvent incorporation [22]. This behavior may lead to the complete dissolution of individual polymeric chains [23]. Introduction of charged groups into a hydrophobic gel, either through hydrolysis or copolymerization with ionic co-monomers, can alter the swelling behavior of gel in water or make it sensitive to ionic strength and pH [24,25].

Swelling and hydrogel properties depend on the synthesis process as well as the amount, nature and location of functional groups. The swelling process can be understood as a balance between electrostatic repulsive forces, and attractive forces, such as hydrogen bonding or hydrophobic interaction. Thus, the gel network can swell "discontinuously" depending on the local composition of the network [26,27]. The ability to synthesize particles with chemical and shape anisotropy has enabled the design of colloidal hydrogels with novel behaviors [28]. For example, particles with alternating non-ionic and polyelectrolyte patches exhibit significant changes in shape triggered by changes in solution pH [29] and gradients in particle thickness have been used to create bending and buckling instabilities [30]. That is, the stimuli–response polymers are interesting because their properties (viscoelasticity, transparency, conductivity, etc.) can be controlled by modifying the structure and organization of the polymers chains [31,32]. These technological requirements have driven the development of methodological advances to synthesize "designer" colloidal hydrogels with a number of desired process and particle characteristics [28].

The purpose of this work is to understand the role and interactions of each component of the particle in a given morphology, in order to control the design and synthesis process of the material. For this aim, three series of functional polymeric latex particles with different morphologies were compared. Two were synthesized in previous works [33,34] and the third was synthesized for this study. The particles were functionalized with different concentrations of acrylic acid and the total number of particles in the system was maintained constant for comparative thermodynamic study. The three different particles morphologies were produced with three variants of semicontinuous process. In order to evaluate the thermodynamic behavior a new thermodynamic tool was developed. This thermodynamic tool allows the interpretation of the volumetric partial properties in terms of the atomic, free volume and hydrations contributions. This approach was taken and adapted from the protein field. Results show different thermodynamic behaviors for each particle morphology, indicating that the carboxylic monomers inside the particle were arranged differently. The obtained results suggest that the sensitivity of the material in its final application can be controlled by particle design [35].

2. Experimental

2.1. List of symbols

BuA	butyl acrylate
MMA	methyl methacrylate
AA	acrylic acid
SDBS	sodium dodecylbenzene sulfonate
T_1	feeding tank 1
T_2	feeding tank 2
ρ	density
u	sound speed
c_L^i	concentration of latex in the step i
c_L^{i+1}	concentration of latex in the step $i+1$
c_L^S	concentration of stock solution of latex
V_C	cell volume
Δv	titration volume
V	3-component system volume
v	specific volume
k_S	specific adiabatic compressibility
t_1	mass fraction of water
t_2	mass fraction of non-polar groups
t_3	mass fraction of polar groups
v_1	specific volume of pure water
k_{S1}	specific adiabatic compressibility of pure water
$v^\circ{}_{P;1}$	specific partial volume of polymeric particles in presence of water (component 1) at infinite dilution
$k_S{}^\circ{}_{P;1}$	specific partial adiabatic compressibility of polymeric particles in presence of water (component 1) at infinite dilution
m_1	mass of water
m_2	mass of non-polar groups
m_3	mass of polar groups
$v_{1;2,3}$	partial volume of water (component 1) in presence of non-polar groups (component 2) and polar groups (component 3)
$v_{2;1,3}$	partial volume of non-polar groups (component 2) in presence of water (component 1) and polar groups (component 3)
$v_{3;1,2}$	partial volume of polar groups (component 3) in presence of water (component 1) and non-polar groups (component 2)
m_P	mass of polymeric particles
$v_{P;1}$	partial volume of polymeric particle in presence of water (component 1)
t_{f2}	mass fraction of non-polar groups in the polymeric particle
t_{f3}	mass fraction of polar groups in the polymeric particle
$v^\circ{}_{P;1/\text{atom}}$	atomic specific partial volume of polymeric particles in presence of water (component 1) at infinite dilution
$v^\circ{}_{P;1/\text{void}}$	free volume contribution to the specific partial volume of polymeric particles in presence of water (component 1) at infinite dilution
$v^\circ{}_{P;1/\text{hyd}}$	hydration specific partial volume of polymeric particles in presence of water (component 1) at infinite dilution
n_h	hydration number
$v^\circ{}_{P;1/\text{shell}}$	hydration specific partial volume of solvent molecules in the hydration shell of polymeric particle
$v^\Delta{}_{2;1,3}$	specific partial volume of non-polar groups (component 2) in presence water (component 1) and polar groups (component 3) at infinite dilution
$v^\Delta{}_{3;1,2}$	specific partial volume of polar groups (component 3) in presence water (component 1) and non-polar groups (component 2) at infinite dilution
$v^\Delta{}_{2;1,3/\text{atom}}$	atomic specific partial volume of non-polar groups (component 2) in presence water (component 1) and polar groups (component 3) at infinite dilution
$v^\Delta{}_{2;1,3/\text{void}}$	free volume contribution to the specific partial volume of non-polar groups (component 2) in presence water (component 1) and polar groups (component 3) at infinite dilution
$v^\Delta{}_{2;1,3/\text{hyd}}$	hydration specific partial volume of non-polar groups (component 2) in presence water (component 1) and polar groups (component 3) at infinite dilution