

Thermodynamics of Fractions and Its Application to the Hydration Study of the Swelling Process in Functionalized Polymer Particles

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A fraction of a three-component system is defined as a thermodynamic entity that groups two components. In this work, the thermodynamics of fractions is developed. The Kern–Weisbrod method has been proposed for two-component systems, but by considering the system as fractionalized, this method can also be employed to calculate the specific partial quantities of the components of a three-component system. This method is used to study the swelling process of functionalized polymeric particles. A series of copolymers of butyl acrylate (BuA) and methyl methacrylate (MMA) functionalized with 0, 5, 10, 15, and 20 wt % of acrylic acid (AA) was synthesized by emulsion polymerization. A thermodynamic study of the polymeric particle swelling as a function of the acrylic acid content and the temperature was carried out. Specific partial volumes, compressibilities, and expansibilities were calculated using density and speed of sound measurements. It was found that the hydration behavior of carboxylic and nonpolar groups of the polymeric particles is thermodynamically driven in accordance with the Gibbs–Duhem equation.

Introduction

Hydration^{1,2} is defined as the modification of the molecular ordering of water around solute molecules and surfaces. The region of modified water structure is commonly referred to as the hydration zone where the properties of water (e.g., density, positional and orientational order, and mobility) are significantly different from their corresponding bulk values. Because compressibility, volume, and expansibility are determined by the composite effect of intra- and intermolecular interactions, their values can be used to gain insight into these interactions.³ These macroscopic observables are sensitive to solute–solvent interactions^{4–7} and therefore have been used to characterize the hydration properties in dilute solutions of solutes such as electrolytes,^{8–12} polyelectrolytes,^{13,14} organic solutes,¹⁵ amino acids,^{3–19} nucleosides and nucleotides,^{20,21} and proteins;^{3,23–28} in processes involving proteins²⁹ or DNA³⁰ and RNA such as denaturation^{31,32} and binding;^{33–37} and in colloid systems such as micellar systems,^{38–42} colloidal silica,⁴³ and polymer colloids.⁴⁴ In this work, the hydration associated with the swelling process of functionalized latex is studied.

Latex is defined as a colloidal dispersion of polymer particles in an aqueous medium that is made by means of an emulsion polymerization reaction.⁴⁵ This is a free-radical-initiated chain polymerization in which a monomer or mixture of monomers is polymerized in the presence of an aqueous solution of a surfactant and an initiator soluble in the continuous phase.

Latex functionalization is performed when modifications of superficial or colloidal properties are sought.

Such functionalization can be carried out by the incorporation of reactive chemical groups (functional groups) provided by an initiator, by a surfactant, or by a functional monomer. The last technique is the most commonly used, having advantages such as the direct incorporation of the monomer by covalent bonding, the control of the quantity of functional groups and the control of the application. Because of the available variety of unsaturated carboxylic acids,⁴⁶ one of the most frequently employed procedures for the functionalization of polymeric chains is carboxylation.

From a scientific and industrial point of view, many of these polymers are important because of their applications. Some examples are ion-exchange resins, hydrogels, and composite materials with specific properties. Indeed, it has been observed that the nanostructure of polymers is dramatically affected by the carboxylation, because of the swelling associated with the presence of these groups.⁴⁷

In the accepted picture of polymer swelling, the ionic groups inside the carboxylated polymer cause these kind of resins to absorb polar solvents; as a result, the material expands or “swells”.⁴⁸ The flexibility of the polymeric chains allows a deformation to occur that gives additional space to the molecules of the solvent inside the structure of the solid. On the other hand, the chains form a molecular three-dimensional network in the solid that can retain solvent in its interior. In the case of a linear carboxylated polymer, covalent bonds between the chains do not exist, and the network arises because of chains that become entangled. This three-dimensional arrangement can vanish if the progressive incorporation of the solvent molecules is not limited when the polymer chains are sufficiently separated.

Several experimental techniques and methods can be used to determine the swelling capacity of functionalized latex particles.^{49–51} For example, in the so-called stepwise alkali/acid

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method,⁵² swelling is thermodynamically explained by interfacial free energy.

The latex is considered in this work as a three-component system. Water is one component, and the other two are the carboxylic and nonpolar groups that form the polymeric particle. A fraction of a three-component system is defined as a thermodynamic entity that groups components. The fractionalized system, consisting the fraction (polymeric particle) and the other component (water), is not a two-component system because it has three degrees of freedom in its composition states: the mass of the third component, the mass of the fraction, and the composition of the fraction. The use of component groups in the thermodynamic analysis was proposed before,³³ but in this work, the thermodynamic definition as well as its properties are developed in order to obtain a rigorous thermodynamic treatment. The hydration of the swelling process is described in terms of specific partial volumes, specific partial adiabatic compressibilities, and specific partial expansibilities, at the limits of infinite dilution of the polymeric particle, and the nonpolar and the carboxylic groups. Information on hydration is obtained by employing two experimental techniques not commonly used in the study of the swelling process of polymeric particles: densimetry and measurement of the speed of sound. The results obtained by the proposed method help to provide insight into the behavior of the polymer in the dispersed media and, therefore, allow one to find the best application of the material or to obtain a better reformulation if the application was already established.

To study the contributions of the polar and nonpolar groups inside the polymeric particle and their effects on the swelling process, thermodynamics tools are developed in this work, as described in the following section. Because these tools are used in other parts of this article, we first present a formal proof (based on the “continuity hypothesis”) of the facts that the values of the partial specific quantities of a system component and the specific thermodynamic properties of the system tend to the values of the specific properties of this component in the pure state when the other components are removed. Then, a reformulation of the Kern–Weisbrod^{53,54} method for two-component systems based on Taylor’s expansions is presented. Subsequently, the three-component system as a fractionalized system and the types of limits at infinite dilution are addressed. The types of limits correspond to the different ways in which the experiments can be carried out. Concluding the section, the application of the Kern–Weisbrod method to a three-component system will be discussed. As it will be seen, it can only be employed in the high-dilution region of the system fraction.

Thermodynamics

Continuity Hypothesis and Some of Its Corollaries.

Consider a thermodynamic multicomponent system containing the components 1, 2, ..., $n - 1$, n . An extensive thermodynamic property J of this system can be expressed mathematically as a function $J^{(n)}$ (where n indicates the number of components) as follows

$$J^{(n)}: D_{TP}^2 \times D_m^n \subset \mathcal{R}^{2+n} \rightarrow J^{(n)}(D_{TP}^2 \times D_m^n) \subset \mathcal{R} \\ (T, P, m_1, m_2, \dots, m_n) \rightarrow J^{(n)}(T, P, m_1, m_2, \dots, m_n) \quad (1)$$

where T is the temperature; P is the pressure, and m_1, m_2, \dots, m_n , are the masses of the n components of the system. In addition, D_{TP}^2 and D_m^n are sets defined as

$$D_{TP}^2 = \{T, P \in \mathcal{R}^2 / (T, P) \in (T_1, T_2) \times (P_1, P_2)\} \quad (2)$$

$$D_m^n = \{(m_1, m_2, \dots, m_n) \in \mathcal{R}^n / m_i \in [0, \infty), \forall i = 1, 2, \dots, n\} \quad (3)$$

The intervals (T_1, T_2) and (P_1, P_2) are the intervals of temperature and pressure over which $J^{(n)}$ is defined. They are open intervals because the interval extremes could be values of temperature and pressure where the system has a phase change and where $J^{(n)}$ would not be continuous. Defining

$$\lim_{(T, P, m_1, m_2, \dots, m_i, \dots, m_n) \rightarrow (T, P, m_1, m_2, \dots, 0^-, \dots, m_n)} J^{(n)}(T, P, m_1, m_2, \dots, m_i, \dots, m_n) \\ \equiv \lim_{(T, P, m_1, m_2, \dots, m_i, \dots, m_n) \rightarrow (T, P, m_1, m_2, \dots, 0^+, \dots, m_n)} J^{(n)}(T, P, m_1, m_2, \dots, m_i, \dots, m_n) \\ = J^{(n)}(T, P, m_1, m_2, \dots, 0, \dots, m_n) \quad (4)$$

it can be assumed that

$$J^{(n)} \in C^\infty(D_{TP}^2 \times D_m^n) \quad (5)$$

That is, $J^{(n)}$ is considered to be an infinite class function in its definition domain. This means that $J^{(n)}$ is a continuous and differentiable function and that each of its successive differentials is also continuous and differentiable. It is typical to employ infinite class functions in physics, and in the concrete case of the thermodynamics, $J^{(n)}$ has always been assumed to be an infinite class function when the domain of definition is an open set. The novelty of eq 5 is that $D_{TP}^2 \times D_m^n$ is not an open set because D_m^n contains its boundary.

Let $h < n$. Then by eq 5

$$\lim_{(T, P, m_1, m_2, \dots, m_h, m_{h+1}, \dots, m_n) \rightarrow (T, P, m_1, m_2, \dots, m_h, 0, \dots, 0)} J^{(n)}(T, P, m_1, m_2, \dots, m_h, m_{h+1}, \dots, m_n) = \\ J^{(n)}(T, P, m_1, m_2, \dots, m_h, 0, \dots, 0) \quad (6)$$

Let $J^{(h)}$ be the function defined as

$$J^{(h)}(T, P, m_1, m_2, \dots, m_h) \equiv J^{(n)}(T, P, m_1, m_2, \dots, m_h, 0, \dots, 0) \quad (7)$$

The function $J^{(h)}$ is an infinite class function because it is defined by eq 7 as a restriction of $J^{(n)}$ in the domain $D_{TP}^2 \times D_m^h \subset D_{TP}^2 \times D_m^n$ where

$$D_m^h = \{(m_1, m_2, \dots, m_h) \in \mathcal{R}^h / m_i \in [0, \infty), \forall i = 1, 2, \dots, h\} \quad (8)$$

and physically it represents the property J of the system containing the components 1, 2, ..., $h - 1$, h . Using eq 7, eq 6 takes the following form with a clearer physical meaning

$$\lim_{(T, P, m_1, m_2, \dots, m_h, m_{h+1}, \dots, m_n) \rightarrow (T, P, m_1, m_2, \dots, m_h, 0, \dots, 0)} J^{(n)}(T, P, m_1, m_2, \dots, m_h, m_{h+1}, \dots, m_n) = \\ J^{(h)}(T, P, m_1, m_2, \dots, m_h) \quad (9)$$

That is, for $h < n$, when m_k tends to zero for every $k > h$, the thermodynamic property J of the n -component system tends to the property J of the system with h components.

The specific partial amount of component i is defined as

$$j_{i;1,2,\dots,i-1,i+1,\dots,n}(T,P,m_1,m_2,\dots,m_n) = \left(\frac{\partial J^{(n)}}{\partial m_i} \right)_{T,P,m_1,m_2,\dots,m_{i-1},m_{i+1},\dots,m_n} \quad (10)$$

By eqs 4 and 5, $j_{i;1,2,\dots,i-1,i+1,\dots,n}$ is also an infinite class function. In eq 10, the amount $j_{i;1,2,\dots,i-1,i+1,\dots,n}$ is defined in the sense that component i is in the presence of the other components of the system. With the notation employed, the symbol $j_{i;1,2,\dots,i-1,i+1,\dots,n}$ means the specific partial amount of component i when it is in the presence of the other components of the system. On the other hand, using eqs 7 and 10 it is possible to demonstrate that

$$\lim_{(T,P,m_1,m_2,\dots,m_h,m_{h+1},\dots,m_n) \rightarrow (T,P,m_1,m_2,\dots,m_h,0,\dots,0)} j_{i;1,2,\dots,i-1,i+1,\dots,n}(T,P,m_1,m_2,\dots,m_n) = j_{i;1,2,\dots,i-1,i+1,\dots,h}(T,P,m_1,m_2,\dots,m_h) \quad (11)$$

Physically, eq 11 means that the specific partial quantities of the first h components of the system with n components tend to the specific partial quantities of the system with h components when the rest of the components are removed from the system.

Recall that $J^{(n)}$ is a homogeneous function of first degree with respect to the variables m_1, m_2, \dots, m_n

$$\frac{1}{m_1 + \dots + m_n} J^{(n)}(T,P,m_1,\dots,m_n) = J^{(n)}(T,P,t_1,\dots,t_n) \quad (12)$$

where t_i

$$t_i = \frac{m_i}{m_1 + m_2 + \dots + m_n} \quad (13)$$

is commonly known as the mass fraction of component i . Because

$$1 = t_1 + t_2 + \dots + t_n \quad (14)$$

the values of t_1, t_2, \dots, t_n are completely specified by only $n - 1$ values of the mass fractions, because one of them can be calculated from the other $n - 1$ values. In this way, a point (t_2, \dots, t_n) of the set

$$D_t^{n-1} = \{(t_2, t_3, \dots, t_n) \in \mathcal{R}^{n-1} / 0 \leq t_2 + \dots + t_n \leq 1, \text{ with } t_i \in [0,1] \forall i = 2, \dots, n\} \quad (15)$$

represents a state of composition of the system. On the other hand, by means of eq 13, $0 \leq t_i < m_i$ and $t_i \in [0, m_i) \subset [0, \infty)$, and so $D_{TP}^2 \times D_t^n \subset D_{TP}^2 \times D_m^n$. Defining the function

$$j^{(n)}: D_{TP}^2 \times D_t^{n-1} \subset \mathcal{R}^{2+(n-1)} \rightarrow j^{(n)}(D_{TP}^2 \times D_t^{n-1}) \subset \mathcal{R} \\ (T,P,t_2,t_3,\dots,t_n) \rightarrow j^{(n)}(T,P,t_2,t_3,\dots,t_n) \quad (16)$$

as

$$j^{(n)}(T,P,t_2,t_3,\dots,t_n) \equiv J^{(n)}(T,P,t_1,t_2,\dots,t_n) \quad (17)$$

the function $j^{(n)}$ is defined as a restriction of $J^{(n)}$ to the domain $D_{TP}^2 \times D_t^{n-1} \subset D_{TP}^2 \times D_m^n$, and for this reason, $j^{(n)} \in C^\infty(D_{TP}^2 \times D_t^{n-1})$. Because $j^{(n)}$ depends only on the composition and does not depend on the size of the system, $j^{(n)}$ is a homogeneous function of zeroth degree with respect to the variables $m_1, \dots,$

m_n . Physically $j^{(n)}$ is the mathematical function that represents the specific quantity j of thermodynamic property J .

Let $t'_i = m_i/(m_1 + m_1 + \dots + m_h)$. By eqs 9 and 17

$$\lim_{(T,P,t_2,t_3,\dots,t_h,t_{h+1},\dots,t_n) \rightarrow (T,P,t'_2,t'_3,\dots,t'_h,0,\dots,0)} j^{(n)}(T,P,t_2,\dots,t_h,t_{h+1},\dots,t_n) = j^{(h)}(T,P,t'_2,t'_3,\dots,t'_h) \quad (18)$$

That is, from the continuity hypothesis (eq 5) and eqs 9, 11, and 18, $J^{(n)}$ contains all of the information about the systems with $h \leq n$ components.

It is interesting to study the special case when $h = 1$, with i being the unique component of the system because the other components have been removed from the system. In a system composed of only component i , the specific partial quantity $j_i^{(1)}$ is equal to the specific amount j_1^* of component i in the pure state.⁵⁵ Then, particularizing eqs 11 and 18 with $h = 1$

$$\lim_{(T,P,t_2,t_3,\dots,t_n) \rightarrow (T,P,0,\dots,0,t_i=1,0,\dots,0)} j_{i;1,2,\dots,i-1,i+1,\dots,n}(T,P,t_2,t_3,\dots,t_i,\dots,t_n) = j_i^*(T,P) \quad (19)$$

and

$$\lim_{(T,P,t_2,t_3,\dots,t_n) \rightarrow (T,P,0,\dots,0,t_i=1,0,\dots,0)} j^{(n)}(T,P,t_2,t_3,\dots,t_i,\dots,t_n) = j_i^*(T,P) \quad (20)$$

From eqs 19 and 20, the specific partial amount of component i and the specific amount of J tend to the specific amount of component i in pure state when the concentrations of the other components tend to zero. Hereafter, the variables T and P will be omitted as it will be understood that they will be kept constant.

Two-Component Systems and Kern–Weisbrod's Extrapolations. Let a two-component system be formed from components 1 and 2. Using Euler's equation for this system, dividing by the total mass of the system, and using eqs 12, 13, and 17, one can write

$$j^{(2)} = j_{1;2}t_1 + j_{2;1}t_2 \quad (21)$$

Using eq 14 for a two-component system, eq 21 can be rewritten as

$$j^{(2)}(T,P,t_2) = j_{1;2}(T,P,t_2) + [j_{2;1}(T,P,t_2) - j_{1;2}(T,P,t_2)]t_2 \quad (22)$$

Because $j^{(2)}$ is an infinite class function in the domain $D_{TP}^2 \times [0, 1]$ at constant temperature and pressure, it is always possible to approximate $j^{(2)}$ by the Taylor's expansion of n th degree around some $t_2 = t_{20}$

$$j^{(2)}(t_2) = P_{j,n}^{t_{20}}(t_2) \quad (23)$$

where the Taylor's expansion of n th order around some $t_2 = t_{20}$ is defined as

$$P_{j,n}^{t_{20}}(t_2) = j^{(2)}(t_{20}) + \left[\frac{\partial j^{(2)}(t_{20})}{\partial t_2} \right]_{T,P} (t_2 - t_{20}) + \frac{1}{2} \left[\frac{\partial^2 j^{(2)}(t_{20})}{\partial t_2^2} \right]_{T,P} (t_2 - t_{20})^2 + \dots + \frac{1}{n!} \left[\frac{\partial^n j^{(2)}(t_{20})}{\partial t_2^n} \right]_{T,P} (t_2 - t_{20})^n \quad (24)$$

It is interesting to study in detail the zeroth and first orders of the Taylor's expansion. From eq 24, the zeroth order is

$$P_{j^{(2)},0}^{t_{20}}(t_2) = j^{(2)}(t_{20}) \quad (25)$$

and the first order is

$$P_{j^{(2)},1}^{t_{20}}(t_2) = j^{(2)}(t_{20}) + \left[\frac{\partial j^{(2)}(t_{20})}{\partial t_2} \right]_{T,P} (t_2 - t_{20}) \quad (26)$$

On the other hand, from the Gibbs–Duhem equation for a two-component system⁵⁶

$$t_1 \left[\frac{\partial j_{1,2}(t_2)}{\partial t_2} \right]_{T,P} + t_2 \left[\frac{\partial j_{2,1}(t_2)}{\partial t_2} \right]_{T,P} = 0 \quad (27)$$

Differentiating eq 22 with respect to t_2 at constant T and P and substituting eq 27 into the result gives the following equation

$$\left[\frac{\partial j^{(2)}(t_2)}{\partial t_2} \right]_{T,P} = j_{2,1}(t_2) - j_{1,2}(t_2) \quad (28)$$

Substituting eqs 21 and 28 into eq 26 then gives

$$P_{j^{(2)},1}^{t_{20}}(t_2) = j_{1,2}(t_{20}) + [j_{2,1}(t_{20}) - j_{1,2}(t_{20})]t_2 \quad (29)$$

Using eq 29, it is possible to experimentally calculate $j_{1,2}$ and $j_{2,1}$ at the concentration $t_2 = t_{20}$ with the Kern–Weisbrod extrapolations^{53,54}

$$j_{1,2}(t_{20}) = \lim_{t_2 \rightarrow 0} P_{j^{(2)},1}^{t_{20}}(t_2) \quad (30)$$

$$j_{2,1}(t_{20}) = \lim_{t_2 \rightarrow 1} P_{j^{(2)},1}^{t_{20}}(t_2) \quad (31)$$

On the other hand, the Taylor's expansion of n th order around $t_{20} = 0$ is defined as

$$P_{j^{(2)},n}^0(t_2) \equiv \lim_{t_{20} \rightarrow 0} P_{j,n}^{t_{20}}(t_2) \quad (32)$$

At zeroth order, from eqs 25 and 32, one obtains

$$P_{j^{(2)},0}^0(t_2) = \lim_{t_{20} \rightarrow 0} j^{(2)}(t_{20}) \quad (33)$$

and substituting eq 20 with $n = 2$ and $i = 1$ into eq 33 gives

$$P_{j^{(2)},0}^0(t_2) = j_1^* \quad (34)$$

That is, the specific property of component 1 in the pure state is the zeroth-order term of the Taylor's expansion around $t_{20} = 0$. Substituting eq 29 into eq 32, the Taylor's expansion around $t_{20} = 0$ at first order is then

$$P_{j^{(2)},1}^0(t_2) = \lim_{t_{20} \rightarrow 0} \{j_{1,2}(t_{20}) + [j_{2,1}(t_{20}) - j_{1,2}(t_{20})]t_2\} \quad (35)$$

Again, by the hypothesis of continuity (eq 5)

$$\lim_{t_{20} \rightarrow 0} j_{2,1}(t_{20}) = j_{2,1}(t_{20}=0) \equiv j_{2,1}^0 \quad (36)$$

The physical meaning of $j_{2,1}^0$ is such that it is defined as a limiting amount at zero concentration. Under these conditions, this limit involves interactions between component 2 and component 1 (but not among the particles or molecules of

component 2). Substituting eqs 19 (with $n = 2$ and $i = 1$) and 36 into eq 35 gives

$$P_{j^{(2)},1}^0(t_2) = j_1^* + (j_{2,1}^0 - j_1^*)t_2 \quad (37)$$

In two-component systems, it is interesting to study the physical meaning of the Taylor's expansion of first order around $t_2 = 0$. When t_2 is small enough ($t_2 \ll 1$) then

$$j^{(2)}(t_2) = P_{j^{(2)},1}^0(t_2) \quad (38)$$

Equation 38 is an analytical definition of the high-dilution region of concentrations. It is interesting to observe that, around $t_{20} = 0$, at the zeroth order of approximation (eq 34) the system is described by component 1 in the pure state. Under these conditions, at first order of approximation and from eq 37, the two-component system is described as a perturbation of the pure state of component 1. That is, when eq 37 holds, the system is composed of component 1 in the pure state, without alterations from the presence of component 2, and component 2 in a special state in which only the interaction with component 1 is involved because the interactions among the molecules or particles of component 2 are not present.

Three-Component Systems. *Fractionalization of a Three-Component System.* Let $J^{(3)}$ be the function of the thermodynamic property J of a three-component system

$$J^{(3)} = J^{(3)}(T, P, m_1, m_2, m_3) \quad (39)$$

The differential of $J^{(3)}$ is then

$$dJ^{(3)} = \left(\frac{\partial J^{(3)}}{\partial m_1} \right)_{m_2, m_3} dm_1 + \left(\frac{\partial J^{(3)}}{\partial m_2} \right)_{m_1, m_3} dm_2 + \left(\frac{\partial J^{(3)}}{\partial m_3} \right)_{m_1, m_2} dm_3 = j_{1,2,3} dm_1 + j_{2,1,3} dm_2 + j_{3,1,2} dm_3 \quad (40)$$

where $j_{1,2,3}$, $j_{2,1,3}$, and $j_{3,1,2}$ are defined by eq 10. Components 2 and 3 will be grouped into a new entity named the fraction of the system. In this section, the three-component system is studied as fractionalized, that is, as composed by component 1 and the fraction f formed by components 2 and 3. The new variables of the system are the mass of component 1 (m_1); the mass of the fraction ($m_f = m_2 + m_3$); and another variable related to the internal composition of the fraction, $t_{f3} = m_3/(m_2 + m_3)$. Mathematically, the variable change is expressed by the functions

$$m_1(m_1, m_f, t_{f3}) = m_1 \quad (41)$$

$$m_2(m_1, m_f, t_{f3}) = m_f(1 - t_{f3}) \quad (42)$$

$$m_3(m_1, m_f, t_{f3}) = m_f t_{f3} \quad (43)$$

The function $J^{(3)}$ takes the following form with the new variables

$$J^{(3)} = J^{(3)}(T, P, m_1, m_f, t_{f3}) \quad (44)$$

and its differential becomes

$$dJ^{(3)} = \left(\frac{\partial J^{(3)}}{\partial m_1} \right)_{m_f, t_{f3}} dm_1 + \left(\frac{\partial J^{(3)}}{\partial m_f} \right)_{m_1, t_{f3}} dm_f + \left(\frac{\partial J^{(3)}}{\partial t_{f3}} \right)_{m_1, m_f} dt_{f3} =$$

$$j_{1,f} dm_1 + j_{f,1} dm_f + \left(\frac{\partial J^{(3)}}{\partial t_{f3}} \right)_{m_1, m_f} dt_{f3} \quad (45)$$

where $j_{1,f}$ and $j_{f,1}$ are defined as

$$j_{1,f}(T, P, t_f, t_{f3}) = \left(\frac{\partial J^{(3)}}{\partial m_1} \right)_{m_f, t_{f3}} \quad (46)$$

$$j_{f,1}(T, P, t_f, t_{f3}) = \left(\frac{\partial J^{(3)}}{\partial m_f} \right)_{m_1, t_{f3}} \quad (47)$$

Both $j_{1,f}$ and $j_{f,1}$ depend on t_{f3} . This fact will be important for specifying the physical meaning of the fraction. The partial derivatives of eqs 40 and 45 are related by⁵⁷

$$\left(\frac{\partial J^{(3)}}{\partial m_1} \right)_{m_f, t_{f3}} = \left(\frac{\partial J^{(3)}}{\partial m_1} \right)_{m_2, m_3} \quad (48)$$

$$\left(\frac{\partial J^{(3)}}{\partial m_f} \right)_{m_1, t_{f3}} = \left(\frac{\partial J^{(3)}}{\partial m_2} \right)_{m_1, m_3} \left(\frac{\partial m_2}{\partial m_f} \right)_{m_1, t_{f3}} + \left(\frac{\partial J^{(3)}}{\partial m_3} \right)_{m_1, m_2} \left(\frac{\partial m_3}{\partial m_f} \right)_{m_1, t_{f3}} \quad (49)$$

$$\left(\frac{\partial J^{(3)}}{\partial t_{f3}} \right)_{m_1, m_f} = \left(\frac{\partial J^{(3)}}{\partial m_2} \right)_{m_1, m_3} \left(\frac{\partial m_2}{\partial t_{f3}} \right)_{m_1, m_f} + \left(\frac{\partial J^{(3)}}{\partial m_3} \right)_{m_1, m_2} \left(\frac{\partial m_3}{\partial t_{f3}} \right)_{m_1, m_f} \quad (50)$$

Using eqs 40, 41–43, and 45, eqs 48–50 take the following form

$$j_{1,f} = j_{1,2,3} \quad (51)$$

$$j_{f,1} = t_{f2} j_{2,1,3} + t_{f3} j_{3,1,2} \quad (52)$$

$$\left(\frac{\partial J^{(3)}}{\partial t_{f3}} \right)_{m_1, m_f} = -m_f(j_{2,1,3} - j_{3,1,2}) \quad (53)$$

where $t_{f2} = m_2/(m_2 + m_3)$. By eq 51, the specific partial amount of component 1 is the same for the system taken as a three-component system and for the system taken as a fractionalized system. From eq 52, $j_{2,1,3}$ and $j_{3,1,2}$ can be interpreted as specific partial amounts in the three-component system or as $t_{f2} \times j_{2,1,3}$ and $t_{f3} \times j_{3,1,2}$ are the contributions to the specific partial quantity of the fraction f . It is interesting to observe that, from eq 39, the function $J^{(3)}$ is a homogeneous function with respect to the variables m_1 , m_2 , and m_3 , but with the new variables (eq 44), it is a homogeneous function with respect to m_1 and m_f . Considering this, the Euler's equation for eq 44 takes the form

$$J^{(3)} = m_1 j_{1,f} + m_f j_{f,1} \quad (54)$$

Differentiation of eq 54 gives

$$dJ^{(3)} = m_1 dj_{1,f} + j_{1,f} dm_1 + m_f dj_{f,1} + j_{f,1} dm_f \quad (55)$$

and setting eqs 45 and 55 equal, using eq 53, and reorganizing, the Gibbs–Duhem equation for the fractionalized system is obtained

$$m_1 dj_{1,f} + m_f dj_{f,1} = m_f(j_{3,1,2} - j_{2,1,3}) dt_{f3} \quad (56)$$

Moreover, if $dt_{f3} = 0$

$$m_1 dj_{1,f} + m_f dj_{f,1} = 0 \quad (57)$$

From eqs 47 and 52, partial specific amounts of fraction f depend on the internal composition of the fraction. By eqs 46 and 51, this internal composition affects the value of partial specific amounts of component 1 as well. Bearing in mind the general definition of the specific partial amount of a component (eq 10), it is possible to establish that the thermodynamic difference between a component and a fraction is that the component does not have internal composition. On the other hand, if the internal composition of the fraction is not varied in a series of experiment ($dt_{f3} = 0$), then by eq 57, the system behaves as a two-component system, and the fraction can be considered as a single component.

Types of Limits of a Three-Component System. As has been shown, for two-component systems, there is only one way to carry out limits of a specific partial quantity at infinite dilution. From eq 19 with $i = 1$ and $n = 2$ and eq 36, this limit is obtained when the amount of one component tends to zero while the amount of the other component remains constant. In three-component systems, there are several types of limits of specific partial quantities at infinite dilution that correspond to different experimental conditions. Limits of type I are defined as the limit of a specific partial quantity when the amount of one component tends to zero while the amounts of the other components remain constant. Type II limits are defined as the limit of a specific partial quantity when the amount of one component tends to zero, the ratio between the amount of this component and the amount of another component is kept constant, and the amount of the third component is also kept constant.

If the amounts of components 1 and 2 are both kept constant ($m_1 = m_1^c$ and $m_2 = m_2^c$) and the amount of component 3 tends to zero, the type I limit for the system is

$$\lim_{m_3 \rightarrow 0}^{\text{type I}} j_{3,1,2} \equiv \lim_{\substack{m_3 \rightarrow 0 \\ m_2 = m_2^c \\ m_1 = m_1^c}} j_{3,1,2}(m_1, m_2, m_3) =$$

$$j_{3,1,2}(m_1, m_2, 0) \equiv j_{3,1,2}^0(m_1, m_2) \quad (58)$$

For components 1 and 2, the type I limits under the above conditions are obtained by eq 19 with $n = 3$, $h = 2$, and $i = 1$ and 2 for components 1 and 2, respectively.

To take type II limits, fraction variables must be employed. The reason is that limiting composition states such as $(m_1, m_f, t_{f3}) = (m_1, 0, t_{f3})$ cannot be represented by variables m_1 , m_2 , and m_3 . If m_1 and the ratio of m_3 to m_2 are maintained as constant, the type II limit of $j_{3,1,2}$ is

$$\lim_{m_3 \rightarrow 0}^{\text{type II}} j_{3,1,2} = \lim_{\substack{m_f \rightarrow 0 \\ t_{f3} = t_{f3}^c \\ m_1 = m_1^c}} j_{3,1,2}(m_1, m_f, t_{f3})$$

$$= \lim_{\substack{t_f \rightarrow 0 \\ t_{f3} = t_{f3}^c}} j_{3,1,2}(t_f, t_{f3}) = j_{3,1,2}(0, t_{f3}) \equiv j_{3,1,2}^{1\Delta}(t_{f3}) \quad (59)$$

The symbol 1Δ in eq 59 means that the amount of component 1 is kept constant. In a similar way for $j_{2,1,3}$, the limit is

$$\lim_{m_3 \rightarrow 0}^{\text{type II}} j_{2,1,3} = j_{2,1,3}(0, t_{f3}) \equiv j_{2,1,3}^{1\Delta}(t_{f3}) \quad (60)$$

As shown in eqs 59 and 60, the type II limits of $j_{3,1,2}$ and $j_{2,1,3}$ depend on the relative concentration of components 2 and 3 (t_{f3}). For $j_{1,2,3}$, this type II limit corresponds to the experimental

situation in which components 2 and 3 are removed from the system, and it is obtained by eq 19 with $n = 3$ and $i = 1$

$$\lim_{\substack{\text{type II} \\ m_3 \rightarrow 0 \\ m_1 = m_1^c}} j_{1,2,3} = \lim_{\substack{t_f \rightarrow 0 \\ t_{f3} = t_{f3}^c}} j_{1,2,3} = j_1^* \quad (61)$$

The following result will be demonstrated

$$\lim_{t_{f3} \rightarrow 0} j_{2,1,3}^{1\Delta} = j_{2,1}^0 \quad (62)$$

Using iterate limits

$$\begin{aligned} \lim_{t_{f3} \rightarrow 0} j_{2,1,3}^{1\Delta} &= \lim_{t_{f3} \rightarrow 0} [\lim_{t_f \rightarrow 0} j_{2,1,3}(t_f, t_{f3})] \\ &= \lim_{t_f \rightarrow 0} [\lim_{t_{f3} \rightarrow 0} j_{2,1,3}(t_f, t_{f3})] \\ &= \lim_{t_f \rightarrow 0} j_{2,1,3}(t_f, 0) \end{aligned} \quad (63)$$

On the other hand, if $t_{f3} = 0$, then $m_3 = 0$, and therefore $t_f = t_2$. Using this result and eq 11 with $n = 3$ and $h = 2$, one obtains

$$\begin{aligned} \lim_{t_f \rightarrow 0} j_{2,1,3}(t_f, 0) &= \lim_{m_2 \rightarrow 0} j_{2,1,3}(m_1, m_2, 0) \\ &= \lim_{m_2 \rightarrow 0} j_{2,1}(m_1, m_2) = j_{2,1}^0 \end{aligned} \quad (64)$$

In a similar way as for eq 62, the following result is demonstrated

$$\lim_{t_{f3} \rightarrow 0} j_{3,1,2}^{1\Delta} = j_{3,1,2}^0 \quad (65)$$

It is interesting to study the limit of the specific partial quantity at infinite dilution of the fraction f of a fractionalized system. This limit is experimentally taken when the amount of the fraction f tends to zero while t_{f3} ($t_{f3} = t_{f3}^c$) and the amount of component 1 ($m_1 = m_1^c$) are both kept constant

$$\begin{aligned} \lim_{\substack{t_{f3} \rightarrow 0 \\ t_{f3} = t_{f3}^c \\ m_1 = m_1^c}} j_{f,1} &= \lim_{\substack{t_f \rightarrow 0 \\ t_{f3} = t_{f3}^c}} j_{f,1}(t_f, t_{f3}) \\ &= j_{f,1}(0, t_{f3}) \equiv j_{f,1}^0(t_{f3}) \end{aligned} \quad (66)$$

The following result is demonstrated using eqs 52, 59, 60, and 66

$$j_{f,1}^0 = t_{f2} j_{2,1,3}^{1\Delta} + t_{f3} j_{3,1,2}^{1\Delta} \quad (67)$$

On the other hand, from eqs 62 and 67

$$\lim_{t_{f3} \rightarrow 0} j_{f,1}^0 = j_{2,1}^0 \quad (68)$$

Kern–Weisbrod Extrapolations in Fractionalized Three-Component Systems. Dividing eq 54 by the total mass of the system and using eqs 12, 13, and 17 with $n = 3$, one obtains

$$j^{(3)} = t_1 j_{1,f} + t_f j_{f,1} \quad (69)$$

where $t_1 = m_1/(m_1 + m_f)$ and $t_f = m_f/(m_1 + m_f)$. As shown in eq 57, when t_{f3} is constant, a fractionalized system behaves as a two-component system. Then, similarly to a two-component systems, at constant t_{f3} , the Taylor's expansion of first order around some $t_f = t_{f0}$ is

$$P_{j^{(3)},1}^{t_{f0}}(t_f, t_{f3}) = j_{1,f}(t_{f0}, t_{f3}) + (j_{f,1}(t_{f0}, t_{f3}) - j_{1,f}(t_{f0}, t_{f3})) t_f \quad (70)$$

Taking the limit in eq 70 as t_{f0} approaches 0 gives

$$P_{j^{(3)},1}^0(t_f, t_{f3}) = \lim_{t_{f0} \rightarrow 0} P_{j^{(3)},1}^{t_{f0}}(t_f, t_{f3}) \quad (71)$$

By using eqs 61 and 66, eq 71 takes the following form

$$P_{j^{(3)},1}^0(t_f, t_{f3}) = j_1^* + (j_{f,1}^0(t_{f3}) - j_1^*) t_f \quad (72)$$

Therefore, $j_{f,1}^0 = j_{f,1}^0(t_{f3})$ can be calculated by using the Kern–Weisbrod extrapolations (eqs 30 and 31) in eq 72. The first-order Taylor's expansion of $j_{f,1}^0$ around some $t_{f3} = t_{f30}$ is

$$P_{j_{f,1}^0,1}^{t_{f30}}(t_{f3}) = j_{f,1}^0(t_{f3}) + \left(\frac{\partial j_{f,1}^0(t_{f3})}{\partial t_{f3}} \right)_{T,P,t_f} (t_{f3} - t_{f30}) \quad (73)$$

In the high-dilution region, the Gibbs–Duhem equation at constant t_f takes the form

$$m_1 \left(\frac{\partial j_1^*}{\partial t_{f3}} \right)_{T,P,t_f} + m_2 \left(\frac{\partial j_{2,1,3}^{1\Delta}}{\partial t_{f3}} \right)_{T,P,t_f} + m_3 \left(\frac{\partial j_{3,2,1}^{1\Delta}}{\partial t_{f3}} \right)_{T,P,t_f} = 0 \quad (74)$$

Because $j_1^* = j_1^*(T, P)$, $(\partial j_1^*/\partial t_{f3})_{T,P,t_f} = 0$. Substituting this result into eq 74 and dividing by the mass of the fraction, gives

$$t_{f2} \left(\frac{\partial j_{2,1,3}^{1\Delta}}{\partial t_{f3}} \right)_{T,P,t_f} + t_{f3} \left(\frac{\partial j_{3,2,1}^{1\Delta}}{\partial t_{f3}} \right)_{T,P,t_f} = 0 \quad (75)$$

Differentiating eq 67 with respect to t_{f3} at constant T and P and substituting eq 75 into the result gives

$$\left[\frac{\partial j_{f,1}^0(t_{f3})}{\partial t_{f3}} \right]_{T,P,t_f} = j_{3,2,1}^{1\Delta}(t_{f3}) - j_{2,1,3}^{1\Delta}(t_{f3}) \quad (76)$$

Substituting eqs 67 and 76 into eq 73 and reorganizing then gives

$$P_{j_{f,1}^0,1}^{t_{f30}}(t_{f3}) = j_{2,1,3}^{1\Delta}(t_{f30}) + [j_{3,1,2}^{1\Delta}(t_{f30}) - j_{2,1,3}^{1\Delta}(t_{f30})] t_{f3} \quad (77)$$

Therefore, $j_{2,1,3}^{1\Delta} = j_{2,1,3}^{1\Delta}(t_{f3})$ and $j_{3,1,2}^{1\Delta} = j_{3,1,2}^{1\Delta}(t_{f3})$ can be calculated by the Kern–Weisbrod extrapolations in eq 77 as

$$j_{2,1,3}^{1\Delta}(t_{f30}) = \lim_{t_{f3} \rightarrow 0} P_{j_{2,1,3}^{1\Delta},1}^{t_{f30}}(t_{f3}) \quad (78)$$

$$j_{3,1,2}^{1\Delta}(t_{f30}) = \lim_{t_{f3} \rightarrow 1} P_{j_{3,1,2}^{1\Delta},1}^{t_{f30}}(t_{f3}) \quad (79)$$

That is, Kern–Weisbrod method can be used in a three-component system, but according to eq 75, it holds only in the high-dilution region of the fraction f .

Experimental Section

Materials. The monomers butyl acrylate (BuA), methyl methacrylate (MMA), and acrylic acid (AA) (National Starch) were commercial grade and were used as received. Sodium dodecylbenzene sulfonate (SDBS) and potassium persulfate (from Aldrich) were reactive grade and were employed as surfactant and initiator, respectively; both were used without further purification. The dispersion medium was distilled water.

Latex Preparation. The carboxylated poly(BuA–MMA) samples were prepared via emulsion polymerization. All reactions were carried out in a semicontinuous reactor consisting of a jacketed reactor and a feeding tank. A continuous flow of pre-emulsion material was ensured by a dosing pump. The reactor consisted of a 1-L stirred glass reactor under a dynamic

flow of N₂ and at a temperature of 70 °C controlled by a thermal bath. The stirring rate was adjusted to 250 rpm. The AA content was varied from 0 to 20 wt %. The pH during the reactions was kept at a value lower than 4 to ensure incorporation of the acrylic acid.^{58–61} The final solid content of the latexes was 10 wt %.

The formulation used to prepare all latexes is listed in Table 1.

TABLE 1: Polymerization Recipes

component	content (g)	
	reactor	feeding tank
butyl acrylate	1.17	0
methyl methacrylate	0.97	41
acrylic acid	0.1	18
potassium sulfate	0.2	0.5
sodium dodecylbenzene sulfonate	0.1	0.1
distilled water	95	443

Density and Ultrasound Speed. A DSA 5000 Anton Paar density and speed of sound analyzer was used. The latex was diluted to concentrations from 1 to 4 wt % with doubly distilled water. The samples were degassed before use. The measurements were made at 25 °C in normal mode of fixed temperature and from 30 to 70 °C in automatic scan mode.

Measurement of Particle Diameter. The hydrodynamic diameter of carboxylated poly(BuA–MMA) was determined by dynamic light scattering (QELS). All samples were diluted to 10 ppm and measured at room temperature using a Malven Autosizer 4800 instrument.

Results

In this work, latex is assumed to be a three-component system formed by a continuous medium, water in this case (component 1), and the nonpolar groups (component 2) and carboxylic groups (component 3) of the polymer chains. On the other hand, this system can be taken as fractionalized, with component 1 being the water and the fraction *f*, the polymeric particle composed of chains with nonpolar and carboxylic groups.

The density, ρ , and the speed of sound, *u*, of the latex samples were measured as functions of *t_f* and the temperature. The specific volume $v^{(3)}$ of the latex sample was calculated from the experimental density as

$$v^{(3)} = \frac{1}{\rho} \quad (80)$$

and the specific adiabatic compressibility was calculated by the equation

$$k^{(3)} = \left(\frac{1}{\rho u} \right)^2 \quad (81)$$

In Figure 1 is shown, as an example, the specific volume and specific compressibility of a latex sample with a carboxylic group content of 5 wt % as a function of mass fraction of water (*t₁*) at different temperatures. A similar behavior was found for the other carboxylic group contents (0, 10, 15, and 20 wt % of AA). The linear behavior of $v^{(3)}$ and $k^{(3)}$ as functions of *t₁* was interpreted assuming that the concentration region studied was in the high-dilution region. For this reason, the Taylor's expansion of first order around *t_f* = 0 was used to describe $v^{(3)}$ and $k^{(3)}$ as functions of the concentration (eqs 37 and 38). Because the purpose is to determine specific partial volume, $v_{f,1}^0$, and specific partial compressibility, $k_{f,1}^0$, of the polymeric particle at infinite dilution from $v^{(3)}$ and $k^{(3)}$ as functions of the

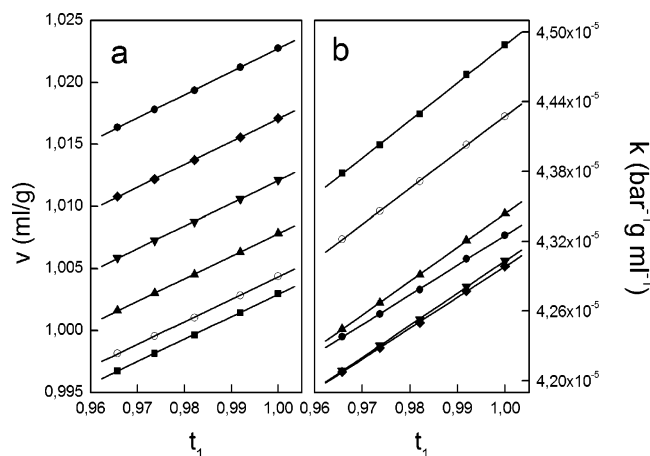


Figure 1. Specific volume $v^{(3)}$ (Figure 1a) and specific adiabatic compressibility $k^{(3)}$ (Figure 1b) of a latex sample with 5% of carboxylic groups (wt % of AA) as a function of the mass fraction of water *t₁* at different temperatures: (■) 25, (○) 30, (▲) 40, (▼) 50, (◆) 60, and (●) 70 °C.

concentration, eq 38 is more useful as a function of *t₁* than as a function of *t_f* because it directly gives $v_{f,1}^0$ and $k_{f,1}^0$ as the intercepts of linear fittings. If eq 38 is used as a function of *t_f*, then an additional operation that increases the experimental error in the final result is needed to calculate $v_{f,1}^0$ and $k_{f,1}^0$ from the slope of the fit.

Using the data of $v^{(3)}$ (Figure 1a), $v_{f,1}^0$ was calculated as the intercept of the linear fit of experimental values of $v^{(3)}$ as a function of *t₁* using the equation

$$v^{(3)}(t_1) = v_{f,1}^0 + (v_1^* - v_{f,1}^0)t_1 \quad (82)$$

where v_1^* is the specific volume of water in the pure state. In the same way $k_{f,1}^0$ was calculated from the data of $k^{(3)}$ (Figure 1b) using the equation

$$k^{(3)}(t_1) = k_{f,1}^0 + (k_1^* - k_{f,1}^0)t_1 \quad (83)$$

where k_1^* is the specific compressibility of water in the pure state. In all of the cases studied (0, 5, 10, 15, and 20 wt % of AA), the correlation coefficient was larger than 0.99. In Figure 2 the calculated values of $v_{f,1}^0$ are shown, and Figure 3 shows the values obtained for $k_{f,1}^0$.

From Figure 2, it is observed that $v_{f,1}^0$ decreases when the amount of carboxylic groups in the polymeric particle is increased (Figure 2a). On the other hand, $v_{f,1}^0$ as a function of the carboxylic group content in the polymer chain decreases faster below 10 wt % of AA content than above. In all cases, $v_{f,1}^0$ increases with the temperature. The specific partial compressibility of the polymer particle at the infinite-dilution limit is shown as a function of the carboxylic group content in Figure 3a and as a function of the temperature in Figure 3b. From Figure 3a, $k_{f,1}^0$ decreases with increasing carboxylic group content, as does $v_{f,1}^0$. The change in the slope of $k_{f,1}^0$ with the carboxylic group content below and above of 10 wt % of AA is sharper than for $v_{f,1}^0$ (Figure 2a). From Figure 3b, one can see that $k_{f,1}^0$ increases with increasing temperature. This observation can be interpreted as indicating that the polymeric particle

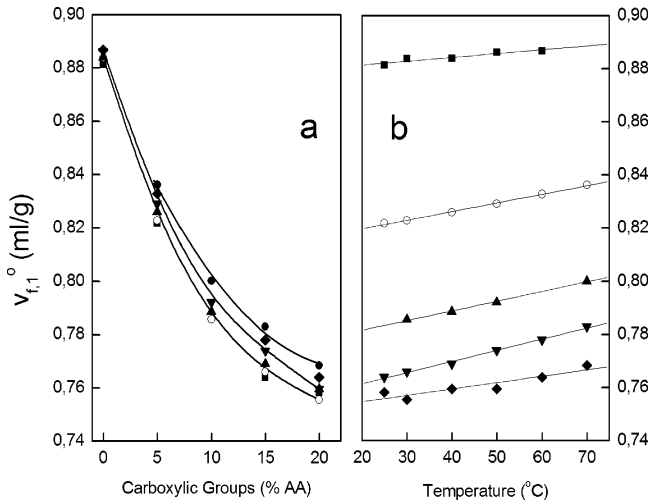


Figure 2. (a) Specific partial volume of polymeric particle at infinite dilution, $v_{f,1}^0$, as a function of carboxylic group content (wt % of AA) at different temperatures (symbols defined in Figure 1). (b) $v_{f,1}^0$ as a function of temperature at different carboxylic group content (wt % of AA): (■) 0, (○) 5, (▲) 10, (▼) 15, and (◆) 20 wt %.

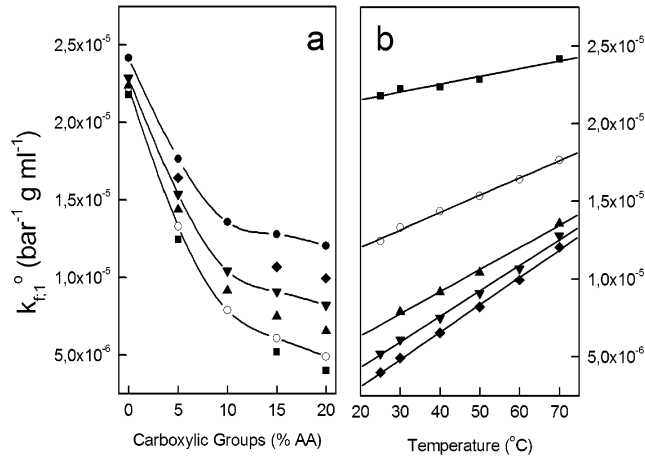


Figure 3. (a) Specific partial adiabatic compressibility of polymeric particle at infinite dilution ($k_{f,1}^0$) as a function of carboxylic group content (wt % of AA) at different temperatures (symbols defined in Figure 1). (b) $k_{f,1}^0$ as a function of temperature at different carboxylic group content (wt % of AA) (symbols defined in Figure 2).

becomes more compressible when the temperature increases, given that the slope of $k_{f,1}^0$ with temperature is higher when the carboxylic group content is increased.

From the data in Figures 2a and 3a, the type II limits of carboxylic and nonpolar groups were calculated. The calculation procedure is explained here for the specific partial volumes only, as the same procedure is employed for the specific partial compressibilities. For each temperature, $v_{f,1}^0$ as a function of t_{f3} was fitted to the following polynomial

$$v_{f,1}^0(t_{f3}) = a + bt_{f3} + ct_{f3}^2 \quad (84)$$

where a , b , and c are the polynomial constants. The Taylor's expansion of $v_{f,1}^0$ at the limit of infinite dilution of the polymeric particle around each studied value of t_{f3i} (i.e., 0, 5, 10, 15, and 20 wt % of AA) is, according to eq 73

$$P_{v_{f,1}^0}^{t_{f3i}}(t_{f3}) = v_{f,1}^0(t_{f3i}) + \left[\frac{\partial v_{f,1}^0(t_{f3i})}{\partial t_{f3}} \right]_{T,P} (t_{f3} - t_{f3i}) \quad (85)$$

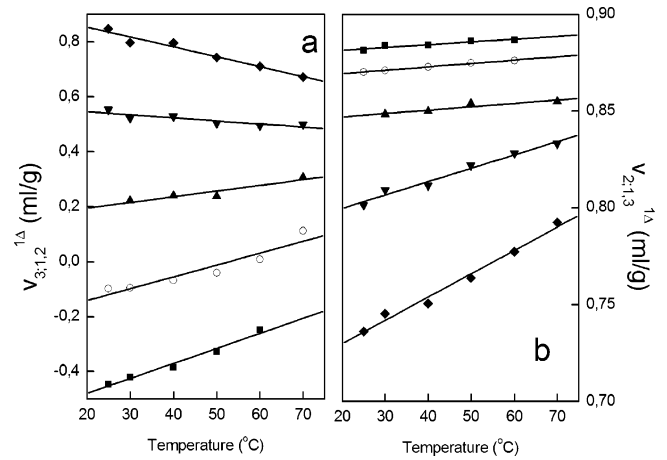


Figure 4. Specific partial volumes of the (a) carboxylic groups and (b) nonpolar groups as functions of temperature at different carboxylic group contents (symbols defined in Figure 2).

From eq 84

$$\left[\frac{\partial v_{f,1}^0(t_{f3i})}{\partial t_{f3}} \right]_{T,P} = b + 2ct_{f3i} \quad (86)$$

Upon substitution of eqs 84 and 86, eq 85 transforms to

$$P_{v_{f,1}^0}^{t_{f3i}}(t_{f3}) = (a - ct_{f3i}^2) + (b + 2ct_{f3i})t_{f3} \quad (87)$$

The amounts $v_{2,1,3}^{1\Delta}$ and $v_{3,1,2}^{1\Delta}$ were calculated by applying eqs 77–79 to eq 87 to give

$$v_{2,1,3}^{1\Delta}(t_{ci}) = \lim_{t_{f3} \rightarrow 0} P_{v_{f,1}^0}^{t_{f3i}}(t_{f3}) = a - ct_{f3i}^2 \quad (88)$$

$$v_{3,1,2}^{1\Delta}(t_{f3i}) = \lim_{t_{f3} \rightarrow 1} P_{v_{f,1}^0}^{t_{f3i}}(t_{f3}) = a + b + c(2t_{f3i} - t_{f3i}^2) \quad (89)$$

In Figure 4, the results obtained for $v_{3,1,2}^{1\Delta}$ and $v_{2,1,3}^{1\Delta}$ are shown. From Figure 4a, one can see that $v_{3,1,2}^{1\Delta}$ can increase or decrease with the temperature when the carboxylic group content changes. At low AA contents, $v_{3,1,2}^{1\Delta}$ increases with the temperature, and at higher contents, it decreases. On the other hand, $v_{3,1,2}^{1\Delta}$ increases with the carboxylic group content. From Figure 4b, it is observed that $v_{2,1,3}^{1\Delta}$ decreases with the AA amount, and its slope with the temperature is positive in all cases studied.

The specific partial adiabatic compressibilities of the carboxylic groups, $k_{3,1,2}^{1\Delta}$, and nonpolar groups, $k_{2,1,3}^{1\Delta}$, are shown as functions of the temperature for different amounts of AA in Figure 5. In both cases, the specific partial adiabatic compressibility increases with the temperature. From Figure 5a, $k_{3,1,2}^{1\Delta}$ increases with the carboxylic group content, being negative in the main part of the range of AA contents studied.

The specific partial expansibilities of the carboxylic groups ($e_{3,1,2}^{1\Delta}$) and nonpolar groups ($e_{2,1,3}^{1\Delta}$) at the limit of infinite dilution of the fraction are defined as

$$e_{3,1,2}^{1\Delta} = \left(\frac{\partial v_{3,1,2}^{1\Delta}}{\partial T} \right)_{P,t_{f3}} \quad (90)$$

and

$$e_{2,1,3}^{1\Delta} = \left(\frac{\partial v_{2,1,3}^{1\Delta}}{\partial T} \right)_{P,t_{f3}} \quad (91)$$

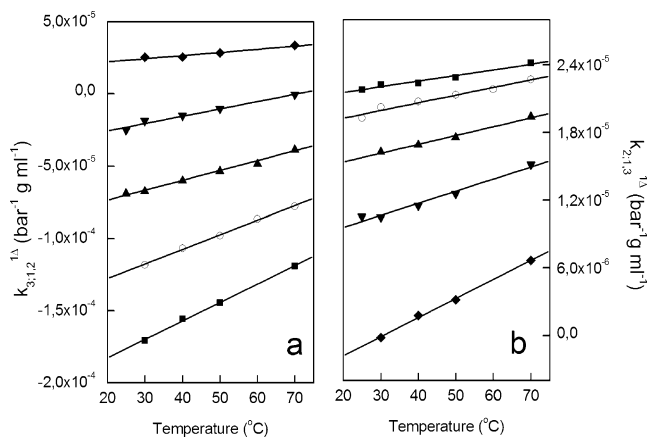


Figure 5. Specific partial adiabatic compressibilities of the (a) carboxylic groups and (b) nonpolar groups as functions of temperature at different carboxylic contents (symbols defined in Figure 2).

and they were calculated from the slopes of linear fits of $v_{3,1,2}^{1\Delta}$ and $v_{2,1,3}^{1\Delta}$ as functions of the temperature using the data of Figure 4.

In Figure 6, the specific partial expansibilities of the polymeric particle, $e_{f,1}^0$; carboxylic groups, $e_{3,1,2}^{1\Delta}$; and nonpolar groups, $e_{2,1,3}^{1\Delta}$, are plotted as functions of the carboxylic group content. It is interesting to observe that $e_{3,1,2}^{1\Delta}$ decreases faster when the AA content increases, going from positive to negative values in the range of AA contents studied. The contribution of the nonpolar groups increases slightly below 10 wt % of AA and exhibits a dramatic increase above this carboxylic group content.

The studied latex samples were assumed to be monodispersed because the polydispersity index in Figure 6b was lower than 1.02 in all cases. This index was calculated by dividing the weight-average diameter by the number-average diameter.

Discussion

As seen in eq 20, a consequence of the continuity hypothesis is that the specific value of a thermodynamic property tends to the specific value of this property in the pure state of a component when the other components of the system are removed. This fact can be observed in Figure 1a,b, where the specific volume and the specific compressibility of the studied latex tend, respectively, to the specific volume and specific compressibility of water when t_f tends to zero.

On the other hand, it is interesting to recall that, when the limit at infinite dilution of the polymeric particles is taken, interactions between polymeric particles vanish, and $j_{f,1}^0$ results only from contributions of the interactions between the water and polymeric particles. In this way, when the type II limits are taken for the nonpolar and carboxylic groups, interactions among these groups on different particles no longer contribute to the properties of the system. That is, type II limits represent a measure of the interactions between the nonpolar and carboxylic groups and water.

The specific partial volume of a particle at infinite dilution, $v_{f,1}^0$, can be interpreted in terms of hydration according to the following relationship^{16,23,25,34,62}

$$v_{f,1}^0 = v_M + \Delta v_h \quad (92)$$

where v_M is the specific intrinsic volume of the solute molecule, which corresponds to the solute domain into which solvent cannot penetrate and makes a positive contribution to $v_{f,1}^0$, and

Δv_h is the specific volume of the hydration, which is the solute-induced change in the solvent volume. The specific intrinsic volume v_M has two contributions

$$v_M = v_c + v_{cav} \quad (93)$$

where v_c is the specific constitutive atomic volume, which, for macromolecules, is equal to the sum of the van der Waals volumes of the constituent atoms, and v_{cav} results from the imperfect atomic packing. Δv_h can be interpreted as

$$\Delta v_h = n_h(v_{sh} - v_{s0}) \quad (94)$$

where n_h is the number of water molecules in the hydration shell and v_{sh} and v_{s0} are the specific partial volumes of water in the hydration shell and in bulk, respectively. On the other hand, according to scaled particle theory, Δv_h can be considered as a sum of two terms^{28,63,64}

$$\Delta v_h = v_T + v_l \quad (95)$$

where v_T is the specific thermal volume of solute, which corresponds to an empty domain around the solute molecule that results from the mutual motions of the solute and solvent molecules. The contribution v_l is the specific interaction volume, which represents the change in solvent volume due to the interactions of each atomic group on the particle surface with surrounding water molecules (electrostriction, hydrophobic interactions, hydrogen bonding) and makes a negative contribution to the total partial specific volume.

By differentiating eq 91 with respect to pressure at constant entropy (S), the specific partial adiabatic compressibility of the particle at the limit of zero concentration can be obtained as^{3,18,19,25,27–29,37}

$$k_{f,1}^0 = \left(\frac{\partial v_{f,1}^0}{\partial P} \right)_S = \left(\frac{\partial v_{cav}}{\partial P} \right)_S + \left(\frac{\partial \Delta v_h}{\partial P} \right)_S = k_{cav} + \Delta k_h \quad (96)$$

where the effect of the pressure on v_c was neglected and k_{cav} and Δk_h are the cavity and hydration contributions, respectively, to $k_{f,1}^0$. As in the case of $v_{f,1}^0$, the contribution k_M is positive and the contribution Δk_h is negative.

On the other hand, by differentiating eq 91 with respect to temperature at constant pressure, the specific partial expansibilities of the particle at the limit of zero concentration and its contributions can be obtained^{16,17,26,29,31} as

$$e_{f,1}^0 = \left(\frac{\partial v_{f,1}^0}{\partial T} \right)_P = \left(\frac{\partial v_{cav}}{\partial T} \right)_P + \left(\frac{\partial \Delta v_h}{\partial T} \right)_P = e_{cav} + \Delta e_h \quad (97)$$

where e_{cav} and Δe_h are the contributions of cavity and hydration, respectively, to $e_{f,1}^0$. Now, differentiating eq 93 with respect to temperature gives¹⁹

$$\Delta e_h = \left(\frac{\partial \Delta v_h}{\partial T} \right)_P = n_h \left[\left(\frac{\partial v_{sh}}{\partial T} \right)_P - \left(\frac{\partial v_{s0}}{\partial T} \right)_P \right] = n_h(e_{sh} - e_{s0}) \quad (98)$$

where the contributions to Δe_h are obtained assuming n_h to be constant and defining e_{sh} as the specific partial expansibility of the water in the hydration shell and e_{s0} as the specific partial expansibility of water in bulk. In this case, e_{cav} is positive, but Δe_h can be positive or negative depending on the difference between e_{sh} and e_{s0} .

The partial volume³² does not change upon the transition of protein molecules from the native state to the molten globule

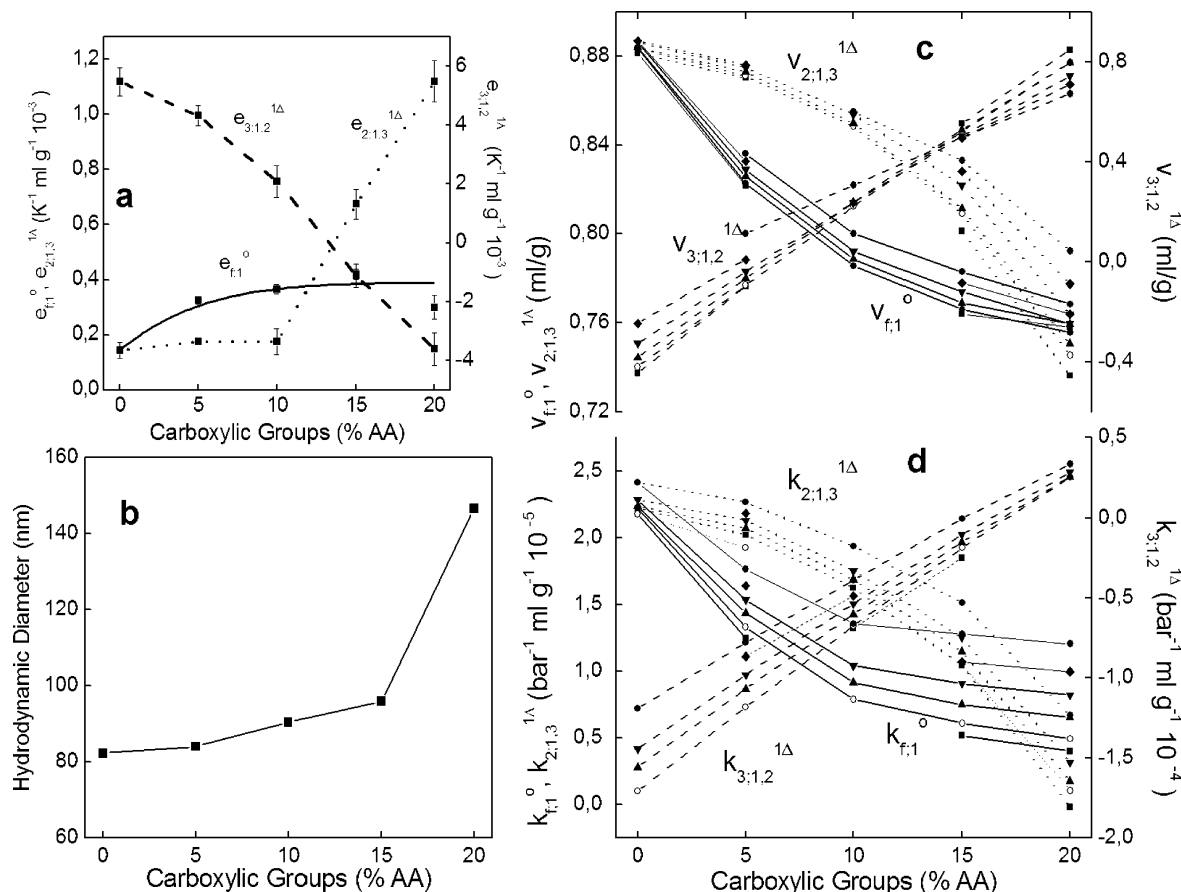


Figure 6. (a) Specific partial expansibilities of the polymeric particle ($e_{f,1}^0$), carboxylic groups ($e_{3,1,2}^{1\Delta}$), and nonpolar groups ($e_{2,1,3}^{1\Delta}$) as functions of the carboxylic group content. (b) Hydrodynamic radius as a function of the AA content at 25 °C. (c) Specific partial volumes of the polymeric particle ($v_{f,1}^0$), carboxylic groups ($v_{3,1,2}^{1\Delta}$), and nonpolar groups ($v_{2,1,3}^{1\Delta}$) as functions of the carboxylic group content at different temperatures (symbols defined in Figure 1). (d) Specific partial compressibilities of the polymeric particle ($k_{f,1}^0$), carboxylic groups ($k_{3,1,2}^{1\Delta}$), and nonpolar groups ($k_{2,1,3}^{1\Delta}$) as functions of the carboxylic group content at different temperatures (symbols defined in Figure 2).

state, whereas the hydrodynamic volume is known to expand by about 35–60%. This discrepancy cannot be explained by a possible change in the molecular shape. Moreover, the magnitudes of the observed changes in the partial volume and compressibility are considerably less than one might expect by analogy to those observed upon the melting of macroscopic organic solids, where a 5–10% volume increase and a 1.5–3-fold compressibility increase are observed. A large amount of water must be incorporated into what is called the hydrodynamic volume of the melted protein molecule. For example, for α -lactalbumin, the molten globule interior is filled with about 270 molecules of water. This number is close to the number of internal polar atoms in the protein, which indicates that a stoichiometric water–polar group interaction might be an essential part of the driving force of the internal hydration and melting processes. On the other hand, the physical properties of the molten globule state cannot be understood and accurately evaluated if the internal water is not taken into consideration. Expansion of hydrodynamic volume upon melting is mainly due to water penetrating into the globule. A large increase in volume and compressibility of solution, which would be expected from the melting itself, is considerably compensated by the negative contribution of the transferred water.

In Figure 6, it can be observed that, when the AA content increases, the average hydrodynamic diameter of the particle is increased (Figure 6b), with a more dramatic change at an AA content of 20 wt %. However, $v_{f,1}^0$ and $k_{f,1}^0$ (Figure 6c,d) exhibit an opposite behavior, where the smaller change in these

properties at high AA content can be explained in terms of the incorporation of water molecules into the structure defined by the hydrodynamic volume.

As previously stated, the polymeric chain is composed of nonpolar and carboxylic groups, and because the carboxylic groups are ionized, an increment of the electrostatic repulsion within the particle occurs when the AA content is increased. This fact causes the polymer chains to disentangle, allowing the entry of water molecules into the particle by osmotic pressure. From Figure 6a, below an AA content of 10 wt %, $e_{2,1,3}^{1\Delta}$ slightly increases because the electrostatic repulsion is causing little effect on the polymer chain disentanglement. In parallel, $e_{3,1,2}^{1\Delta}$ decreases, and this fact can be explained in terms of the incorporation into the particle of a low number of water molecules. When the behaviors of both $e_{3,1,2}^{1\Delta}$ and $e_{2,1,3}^{1\Delta}$ are combined, by eq 52, an increment in $e_{f,1}^0$ is obtained. At higher AA contents, $e_{2,1,3}^{1\Delta}$ quickly increases because the electrostatic repulsion is sufficient to cause a strong effect on polymer chain disentanglement.

By eq 62, when the carboxylic group content in the particle tends to zero

$$\lim_{t_B \rightarrow 0} v_{3,1,2}^{1\Delta} = v_{3,1,2}^0 \quad (99)$$

$$\lim_{t_B \rightarrow 0} k_{3,1,2}^{1\Delta} = k_{3,1,2}^0 \quad (100)$$

From Figure 6c,d, $v_{3,1,2}^0$ and $k_{3,1,2}^0$ are both negative. That is, for

the carboxylic groups at the limit of zero concentration of these groups in the particle, the hydration effects are more important than the cavity effects. An analogous result was found for substances of low molecular weight, where the partial molar adiabatic compressibility primarily reflects solvent hydration changes.^{17,19} This fact can be explained if, at this concentration limit ($t_{f3} = 0$), the carboxylic groups are found on the surface of the particle. For $t_{f3} > 0$, from Figure 6c,d, $v_{3;1,2}^0 < v_{3;1,2}^{1\Delta}$ and $k_{3;1,2}^0 < k_{3;1,2}^{1\Delta}$. That is, the specific partial volume and compressibility of the carboxylic groups become less negative. Both changes can be due only to an increment in the cavity terms (v_{cav} and k_{cav} in eqs 93 and 96, respectively), as it was shown that it is not possible to consider a loss of hydration. On the other hand, the above increments in the cavity terms can be interpreted as the carboxylic groups increasingly being found in the interior of the particle. At 5 wt % of AA, the carboxylic groups are mainly found on the surface as $v_{3;1,2}^{1\Delta}$ and $k_{3;1,2}^{1\Delta}$ are both negative. Then, $v_{3;1,2}^{1\Delta}$ becomes positive as the carboxylic groups become strongly hydrated because $k_{3;1,2}^{1\Delta}$ is negative for all of the AA content range studied.

Conclusions

The facts that the specific value of an extensive thermodynamic property tends to the specific value of the same property in the pure state of a component when other components of the system are removed and that specific partial quantity of a component tends to the specific value of the same quantity in the pure state of this component under the same circumstances are usually taken as observations or experimental facts, and they are introduced⁶⁵ as empirical elements in the thermodynamics. It is typical to take infinite class functions in all disciplines of physics, but the novelty of the continuity hypothesis (eq 5) is that functions in thermodynamics are taken as infinite class functions, even in the case when the amount of some component is zero. Consequently, the above empirical facts can be derived from thermodynamics without the necessity of introducing them empirically (eqs 19 and 20).

Another consequence of the continuity hypothesis is that, in two-component systems, the high-dilution region of a thermodynamic property $j^{(2)}$ can be analytically defined as the concentration region where $j^{(2)}$ is described by the Taylor's expansion of first order around $t_2 = 0$. It is very interesting to notice that the definition of the high-dilution region is related to the system and the thermodynamic property. That is, by this definition, each thermodynamic property $j^{(2)}$ has its own high-dilution region. If this region depends only on the system and not on the employed thermodynamic property, open formal problem in thermodynamics remains.

In the usual formalization of the Kern–Weisbrod method,^{53,54} eqs 26 and 29 are geometrically interpreted as the tangent to the curve of the function $j^{(2)}$ at the point t_{20} . In this way, $j_{1,2}(t_{20})$ and $j_{2,1}(t_{20})$ are calculated taking the Kern–Weisbrod extrapolations on the tangent at $t_{20} = 0$ and at $t_{20} = 1$ (or $t_{10} = 0$), respectively. Formally, this interpretation causes problems at the limit $t_{20} = 0$ because eq 37 would describe the behavior of the tangent, but experimentally, the Kern–Weisbrod extrapolations would be taken using points of $j^{(2)}$. It is necessary to empirically assume that, in this region, the second derivative of $j^{(2)}$ with respect to t_2 is zero for the tangent to approach the curve in a suitable way. That is, with this formalization, the Kern–Weisbrod method becomes an empirical method in the high-dilution region. With the exposition detailed in this paper, the above formal problems around $t_{20} = 0$ do not appear to give this method convenient thermodynamic rigor. On the other

hand, by eq 27, the Kern–Weisbrod method can be used in two-component systems at all concentrations. From eq 75, this method is only applicable at the limit of infinite dilution of the fraction in three-component systems.

With the methodology presented and the experimental techniques employed, the swelling process of functionalized polymeric particles was studied. It was also found that the hydration effect plays an important role in this process. Methodologically, the three-component system was studied in two steps. The first step was to take the system as a two-component system formed by the water and a fraction of the system (polymeric particle). In the second step, using the results of the first step, the thermodynamic properties of the fraction components were calculated. The system studied is a clear example where the fraction is under high-dilution conditions and the components of the fraction exhibit a more complicated behavior in their thermodynamic properties. It is interesting to note that the Gibbs–Duhem equation (eq 75) holds for the effect of the hydration of the components of the fraction at infinite dilution of the particle. In other words, the hydration behavior of the components of the fraction cannot be studied separately because the behavior of one component is made dependent on the behavior of the other one.

It was also shown that $e_{3;1,2}^{1\Delta}$ as a function of the AA content decreases until it reaches negative values. A similar behavior¹⁹ was found for the contribution of the carboxylic groups to the specific partial expansibility of α,β -aminocarboxylic acids in water and deuterium. This contribution was found to decrease with increasing temperature, taking negative values above 40 °C. This fact means (by eq 98) that the specific partial thermal expansibility of the water molecules surrounding the carboxylic groups at these temperatures is lower than the specific partial thermal expansibility of the water molecules in bulk. That is, for high AA contents, the state of the water surrounding the carboxylic groups is very different from the state of water in the bulk. On the other hand, considering eq 75, in the case of the polymeric particles studied, the decrease of $e_{3;1,2}^{1\Delta}$ to negative values can be explained by the fast increase of $e_{2;1,3}^{1\Delta}$ above 10 wt % of AA (Figure 6a). This last increase is caused by the electrostatic repulsion between the carboxylic groups. This fact reveals the relevance of the connection between the thermodynamic behaviors of the different groups of the system studied. In the case of specific partial volumes and compressibilities, this connection indicates that the decreasing of $v_{2;1,3}^{1\Delta}$ and $k_{2;1,3}^{1\Delta}$ with the AA content by hydration increases the values of $v_{3;1,2}^{1\Delta}$ and $k_{3;1,2}^{1\Delta}$ above $v_{3;1,2}^0$ and $k_{3;1,2}^0$. This could be interpreted in the sense that the hydration of the nonpolar groups causes an increase in the cavity contributions to $v_{3;1,2}^{1\Delta}$ and $k_{3;1,2}^{1\Delta}$. In light of this result, the hydration behavior of the polymeric particle results from two contributions. The faster decrease of $v_{f,1}^0$ and $k_{f,1}^0$ below 10 wt % of AA is due to the negative contributions of the carboxylic groups, and the slower decrease above this AA content is produced by the balance between (Figure 6c,d) the increase of the contributions of the carboxylic groups and the decrease of the contributions of the nonpolar groups. Finally, as observed in Figure 6b, at 20 wt % of AA, the hydrodynamic diameter increases by around 80% with respect to the value at 0 wt % of AA. This fact can be interpreted as indicating that a great number of water molecules are incorporated into the structure formed by the hydrodynamic volume. Keeping in mind the strong hydration reflected in the behavior of $v_{2;1,3}^{1\Delta}$ and $k_{2;1,3}^{1\Delta}$, it is possible to consider that, at this AA content, the polymer chains are in a state close to being dissolved into the water.

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