Chapter 4

Determination of Thermodynamic Partial Properties in Multicomponent Systems by Titration Techniques

Mónica Corea, Jean-Pierre E. Grolier and
José Manuel del Río

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.69706

Abstract

Thermodynamic experimental techniques using titration are usually employed to study the interaction between solutes in a diluted solution. This chapter deals with the underlying thermodynamic framework when titration technique is applied with densimetry, sound speed measurement and isothermal titration calorimetry. In the case of partial volumes and partial adiabatic compressibilities, a physical interpretation is proposed based upon atomic, free volume and hydration contributions.

Keywords: thermodynamics, molar partial volumes, molar partial adiabatic compressibilities, molar partial enthalpies, densimetry, sound velocity, isothermal titration calorimetry

1. Introduction

The purposes of this chapter are twofold. First, the thermodynamics fundaments are studied in detail to determine experimentally, calculate and interpret thermodynamic partial molar properties using different titration techniques. Second, the postgraduate students are provided with the necessary thermodynamic background to extract behavioural trends from experimental techniques including densimetry, sound speed measurement and isothermal titration calorimetry.

The first concept introduced in this chapter is "thermodynamic description". It is defined as a set of variables employed to define thermodynamically the studied system. For example, a description by components of a multicomponent system is:

$$J = J(n_1, n_2, n_3) \tag{1}$$

where J is an extensive thermodynamic property; n_1, n_2 and n_3 are the number of moles of components 1, 2 and 3. Other type of thermodynamic description is in terms of the concept of "fraction of a system". A fraction of a system is a thermodynamic entity, with internal composition, which groups several components. For example, the above-mentioned system can be considered as being composed of the component 1, and a fraction F grouping components 2 and 3. In this way, J can be written as:

$$J = J(n_1, n_F, x_{f3}) \tag{2}$$

where n_F is the total number of moles of the fraction F and x_{f3} is a variable related to the composition of the fraction. Depending on the system, one can choose the more adequate description. For example, in a liquid mixture, a description by components (Eq. (1)) can be suitable. Other systems as those shown in **Figure 1** could be better described in terms of fractions.

Figure 1A shows a system composed of the solvent (component 1), solute A (component 2) and solute B (component 3). This system will be described in this chapter using a description by fractions representing a "complex solute" composed of solutes A and B (see **Figure 1B**). This description is appropriate to use in conditions of infinite dilution and dilute solutions. Other example (see **Figure 1C** and **D**) is a functionalized latex particle. A latex is a system composed of polymeric particles dispersed in a solvent. In a functionalized latex, particles are composed of non-polar groups and functional groups (usually polar groups). In this case, a description by components expressed in Eq. (1) and visualized in **Figure 1C** is very difficult to use and it is more convenient to consider a fraction (polymeric particle) composed of non-polar groups (component 2) and polar groups (component 3). **Figure 1D** shows a sketch of this description.

When different descriptions are considered for a system, we have to reconsider the relation between the description and the thermodynamic object studied. In principle, one might think that all descriptions are equivalent. But this is not true because not all descriptions can retain all

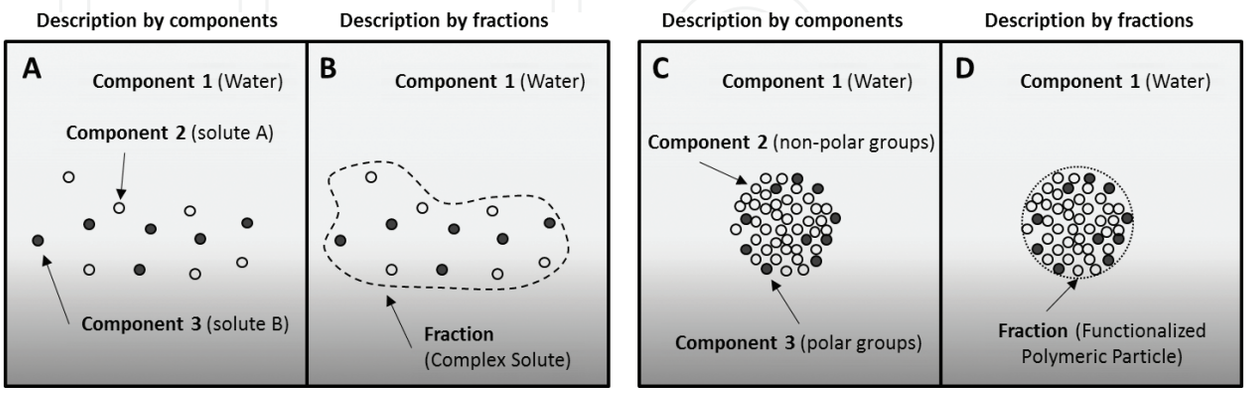

Figure 1. Examples of different descriptions in two systems. (A) and (B) are several solutes in a solvent. (C) and (D) are a functionalized latex with polar groups.

features of a thermodynamic system. For example, it is not possible to speak about thermodynamic partial properties at infinite dilution in multicomponent systems. This fact should not be surprising because in differential geometry [1], there is the same problem associated with the relation between a parametrization and a geometric object. Let's consider, for example, the sphere of radius equal to one, and a parametrization is:

$$\mathbf{X_1}(x, y) = \left(x, y, \sqrt{1 - (x^2 + y^2)}\right) \tag{3}$$

The problem with this parametrization is that it only covers the top half of the sphere. In addition, it is not differentiable in the points of the sphere's equator. Other possibility is:

$$\mathbf{X_2}(x, y) = \left(x, y, -\sqrt{1 - (x^2 + y^2)}\right) \tag{4}$$

But, it only covers the lower half of the sphere and neither is differentiable in points of the sphere's equator. Even if we consider a combination of $\mathbf{X}_1$ and $\mathbf{X}_2$, we have the problem of the lack of differentiability in the points of the sphere's equator. Another possible parametrization is:

$$\mathbf{X}_3(\theta, \varphi) = (\sin\theta\cos\varphi,\ \sin\theta\sin\varphi,\ \cos\theta) \tag{5}$$

where θ is the colatitude (the complement of the latitude) and φ the longitude. $\mathbf{X}_3$ covers the whole surface of the sphere and it is also differentiable in all points. For this reason, it contains more information about the sphere (geometric object) than $\mathbf{X}_1$ and $\mathbf{X}_2$. Backing to thermodynamics, in the same case than for $\mathbf{X}_3$, the partial molar properties at infinite dilution cannot be obtained and manipulated using the description by components, and it is necessary to use the description by fractions.

The other concept also introduced in this chapter is the "interaction between components of a system". The first principle of thermodynamics establishes the way, in which systems interact between them and/or with surroundings. In this case, we are interested in the interaction inside the systems and this cannot be interpreted macroscopically using the first principle of thermodynamics. With the concept of interaction between components, we can define mathematically a dilute solution and characterize its thermodynamic behaviour in terms of molar partial properties. In addition to this, we will consider the partial molar properties at infinite dilution. These properties are essential in studies of polymeric particles because they contain the information about the interactions inside the particles. These interactions determine the architecture and final application of the particle.

2. Mathematical fundaments

In this section, some mathematical tools are presented such as changes of variable, changes of size, the Euler theorem and limits in multivariable functions. Variable changes will allow us to relate partial properties of different descriptions. Changes of size are the processes underlying

the extensivity and non-extensivity of thermodynamic properties, which will be mathematically implemented by the concept of homogeneity. The Euler's theorem will be treated in the more general form, and in its demonstration we will avoid some aspects, which remain unclear in the versions of the textbooks of Callen [2] and Klotz and Rosenberg [3].

2.1. Changes of variable

Let f be the function defined as:

$$f = f(x_1, x_2, x_3) \tag{6}$$

The gradient of f with respect to the variables x_1, x_2 and x_3 is the vector:

$$\nabla f(x_1, x_2, x_3) = \begin{bmatrix} \left(\frac{\partial f}{\partial x_1}\right)_{x_2, x_3} \\ \left(\frac{\partial f}{\partial x_2}\right)_{x_1, x_3} \\ \left(\frac{\partial f}{\partial x_3}\right)_{x_1, x_2} \end{bmatrix} \tag{7}$$

If we consider the change of variable:

$$\begin{cases} x_1 = x_1(y_1, y_2, y_3) \\ x_2 = x_2(y_1, y_2, y_3) \\ x_3 = x_3(y_1, y_2, y_3) \end{cases} \tag{8}$$

the function f will take the form:

$$f = f(y_1, y_2, y_3) \tag{9}$$

where its gradient will be:

$$\nabla f(y_1, y_2, y_3) = \begin{bmatrix} \left(\frac{\partial f}{\partial y_1}\right)_{y_2, y_3} \\ \left(\frac{\partial f}{\partial y_2}\right)_{y_1, y_3} \\ \left(\frac{\partial f}{\partial y_3}\right)_{y_1, y_2} \end{bmatrix} \tag{10}$$

Our interest is to relate the partial derivatives with respect to the variables x_1, x_2 and x_3 given in Eq. (7) with the partial properties with respect to y_1, y_2 and y_3 given in Eq. (10). From Eq. (8), the total differential of x_1 is:

$$dx_1 = \left(\frac{\partial x_1}{\partial y_1}\right)_{y_2, y_3} dy_1 + \left(\frac{\partial x_1}{\partial y_2}\right)_{y_1, y_3} dy_2 + \left(\frac{\partial x_1}{\partial y_3}\right)_{y_1, y_2} dy_3 \tag{11}$$

Using dx_1 given by Eq. (11) and similarly with equations for dx_2 and dx_3, we can write:

$$\begin{bmatrix} dx_1 \\ dx_2 \\ dx_3 \end{bmatrix} = \mathbf{T}\begin{pmatrix} x_1\ x_2\ x_3 \\ y_1\ y_2\ y_3 \end{pmatrix}\begin{bmatrix} dy_1 \\ dy_2 \\ dy_3 \end{bmatrix} \tag{12}$$

where the matrix **T** is:

$$\mathbf{T}\begin{pmatrix} x_1\ x_2\ x_3 \\ y_1\ y_2\ y_3 \end{pmatrix} = \begin{bmatrix} \left(\frac{\partial x_1}{\partial y_1}\right)_{y_2,y_3} & \left(\frac{\partial x_1}{\partial y_2}\right)_{y_1,y_3} & \left(\frac{\partial x_1}{\partial y_3}\right)_{y_1,y_2} \\ \left(\frac{\partial x_2}{\partial y_1}\right)_{y_2,y_3} & \left(\frac{\partial x_2}{\partial y_2}\right)_{y_1,y_3} & \left(\frac{\partial x_2}{\partial y_3}\right)_{y_1,y_2} \\ \left(\frac{\partial x_3}{\partial y_1}\right)_{y_2,y_3} & \left(\frac{\partial x_3}{\partial y_2}\right)_{y_1,y_3} & \left(\frac{\partial x_3}{\partial y_3}\right)_{y_1,y_2} \end{bmatrix} \tag{13}$$

From (6) and using (7), the total differential of f can be expressed as:

$$df = \left(\frac{\partial f}{\partial x_1}\right)_{x_2,x_3} dx_1 + \left(\frac{\partial f}{\partial x_2}\right)_{x_1,x_3} dx_2 + \left(\frac{\partial f}{\partial x_3}\right)_{x_1,x_2} dx_3 = [\nabla f(x_1,x_2,x_3)]^{\mathrm{T}}\begin{bmatrix} dx_1 \\ dx_2 \\ dx_3 \end{bmatrix} \tag{14}$$

where the symbol "T" indicates "transpose". From Eq. (9) using Eq. (10), the differential of f can be written as:

$$df = \left(\frac{\partial f}{\partial y_1}\right)_{y_2,y_3} dy_1 + \left(\frac{\partial f}{\partial y_2}\right)_{y_1,y_3} dy_2 + \left(\frac{\partial f}{\partial y_3}\right)_{y_1,y_2} dy_3 = [\nabla f(y_1,y_2,y_3)]^{\mathrm{T}}\begin{bmatrix} dy_1 \\ dy_2 \\ dy_3 \end{bmatrix} \tag{15}$$

Equaling (15) to (14) and using (12):

$$[\nabla f(y_1,y_2,y_3)]^{\mathrm{T}} = [\nabla f(x_1,x_2,x_3)]^{\mathrm{T}}\mathbf{T}\begin{pmatrix} x_1\ x_2\ x_3 \\ y_1\ y_2\ y_3 \end{pmatrix} \tag{16}$$

Remembering that **x** being a vector and **A** a matrix, then $(x^T A)^T = A^T x$, and taking the transpose in both sides of (16):

$$\nabla f(y_1,y_2,y_3) = \left[\mathbf{T}\begin{pmatrix} x_1\ x_2\ x_3 \\ y_1\ y_2\ y_3 \end{pmatrix}\right]^{\mathrm{T}}\nabla f(x_1,x_2,x_3) \tag{17}$$

Eq. (17) relates the vector gradient with respect to the variables (x_1, x_2, x_3) to the vector gradient with respect to the variables (y_1, y_2, y_3), and it will allow us to express the partial properties in two different descriptions.

2.2. Changes of size

In this paragraph, the process of size change in thermodynamic systems is analyzed. The behaviour of systems in a size change has consequences on the behaviour or nature of the thermodynamic properties as well as on the form of the thermodynamic equations of the system. **Figure 2** shows a visualization of this process in both directions: increasing and reduction.

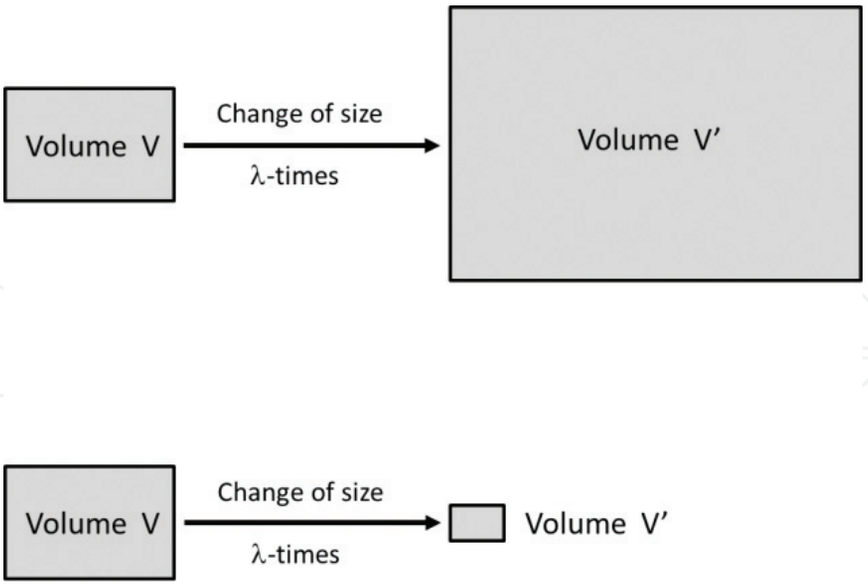

Figure 2. Sketch of the change of size (increasing and reduction) of a system with volume *V*.

From **Figure 2**, it is clear that being V the volume, N the number of moles and U the internal energy, the configuration of this system is under increasing size λ times:

$$\begin{aligned} V &\xrightarrow{\lambda-times} V' = \lambda V \\ N &\xrightarrow{\lambda-times} N' = \lambda N \\ U &\xrightarrow{\lambda-times} U' = \lambda U \end{aligned} \tag{18}$$

Thermodynamic properties, which transform accordingly to (18), depend on the size of the system and are named extensive variables. Not all thermodynamic variables transform according to Eq. (18). An example is the molar fraction of the component 2 (x_2) in a two-component system. We can see this formally in the following way. For a two-component system:

$$\begin{aligned} N_1 &\xrightarrow{\lambda-times} N'_1 = \lambda N_1 \\ N_2 &\xrightarrow{\lambda-times} N'_2 = \lambda N_2 \end{aligned} \tag{19}$$

and x_2 transforms as:

$$x_2 \xrightarrow{\lambda-times} x'_2 = \frac{N'_2}{N'_1 + N'_2} = \frac{\lambda N_2}{\lambda N_1 + \lambda N_2} = \frac{N_2}{N_1 + N_2} = x_2 \tag{20}$$

That is, the molar fraction of the component 2 is independent of the system size. Properties, which remain constant upon size change, are named intensive properties. Other thermodynamic properties with such characteristics are temperature, pressure, pH and concentration c_2 ($c_2 = N_2/V$). It is also interesting to look at the behaviour of functions, which depend on thermodynamic variables (intensive and/or extensive), in a size change. Let, for example, the function f be given by $f = f(T, P, N_1, N_2, \ldots)$. For particular values of the variables T_0, P_0, N_{01}, N_{02}, …, the function f takes the value f_0, and in a change of size:

$$\begin{aligned} &T_0 \xrightarrow{\lambda-times} T'_0 = T_0 \\ &P_0 \xrightarrow{\lambda-times} P'_0 = P_0 \\ &N_{01} \xrightarrow{\lambda-times} N'_{01} = \lambda N_{01} \\ &N_{02} \xrightarrow{\lambda-times} N'_{02} = \lambda N_{02} \\ &\ldots \\ &f_0 \xrightarrow{\lambda-times} f'_0 \end{aligned} \tag{21}$$

If $f'_0 = lf_0$, the function will behave as an extensive property. This concept is mathematically implemented as:

$$f(T, P, \lambda N_1, \lambda N_2, \ldots) = \lambda f(T, P, N_1, N_2, \ldots) \tag{22}$$

In this case, f is a homogeneous function of one degree. If $f'_0 = f_0$, f will behave as an intensive property. Mathematically, f is expressed as a homogeneous function of zero degree as:

$$f(T, P, \lambda N_1, \lambda N_2, \ldots) = f(T, P, N_1, N_2, \ldots) \tag{23}$$

2.3. Euler´s theorem

Let $f = f(x_1, x_2, \ldots; y_1, y_2, \ldots)$ be a function, which is a homogeneous function of one degree with respect to the variables $y_1, y_2, \ldots$:

$$f(x_1, x_2, \ldots; \lambda y_1, \lambda y_2, \ldots) = \lambda f(x_1, x_2, \ldots; y_1, y_2, \ldots) \tag{24}$$

Then,

$$f = \left(\frac{\partial f}{\partial y_1}\right)_{x_1, x_2, \ldots; y_2, y_3, \ldots.} y_1 + \left(\frac{\partial f}{\partial y_2}\right)_{x_1, x_2, \ldots; y_1, y_3, \ldots.} y_2 + \ldots. \tag{25}$$

The demonstration is as follows. The differential with respect to λ in the left side of (24) is:

$$\begin{aligned} \frac{df(x_1, x_2, \ldots; \lambda y_1, \lambda y_2, \ldots)}{d\lambda} = &\left(\frac{\partial f(x_1, x_2, \ldots; \lambda y_1, \lambda y_2, \ldots)}{\partial x_1}\right)_{x_2, x_3, \ldots; \lambda y_1, \lambda y_2, \ldots} \\ &\frac{dx_1}{d\lambda} + \left(\frac{\partial f(x_1, x_2, \ldots; \lambda y_1, \lambda y_2, \ldots)}{\partial x_2}\right)_{x_1, x_3, \ldots; \lambda y_1, \lambda y_2, \ldots} \\ &\frac{dx_2}{d\lambda} + \left(\frac{\partial f(x_1, x_2, \ldots; \lambda y_1, \lambda y_2, \ldots)}{\partial(\lambda y_1)}\right)_{x_1, x_2, \ldots; \lambda y_2, \lambda y_3, \ldots} \\ &\frac{d(\lambda y_1)}{d\lambda} + \left(\frac{\partial f(x_1, x_2, \ldots; \lambda y_1, \lambda y_2, \ldots)}{\partial(\lambda y_2)}\right)_{x_1, x_2, \ldots; \lambda y_1, \lambda y_3, \ldots} \frac{d(\lambda y_2)}{d\lambda} + \ldots \end{aligned} \tag{26}$$

For the sets of variables $x_1, x_2, \ldots$ and $y_1, y_2, \ldots$, we obtain respectively that:

$$\frac{dx_1}{d\lambda} = \frac{dx_2}{d\lambda} = \ldots = 0 \tag{27}$$

$$\frac{d(\lambda y_1)}{d\lambda} = y_1, \qquad \frac{d(\lambda y_2)}{d\lambda} = y_2, \quad \ldots \tag{28}$$

The following step in this demonstration is different from the step proposed in other textbooks [2, 3]. The partial derivative of f with respect to (λy_1) can be expressed as:

$$\left(\frac{\partial f(x_1, x_2, \ldots; \lambda y_1, \lambda y_2, \ldots)}{\partial(\lambda y_1)}\right)_{x_1, x_2, \ldots; \lambda y_2, \lambda y_3, \ldots}$$

$$= \lim_{\Delta \to 0} \frac{f(x_1, x_2, \ldots; \lambda y_1 + \Delta, \lambda y_2, \ldots) - f(x_1, x_2, \ldots; \lambda y_1, \lambda y_2, \ldots)}{\Delta} \tag{29}$$

Considering that f is a homogeneous function of one degree with respect to the variables y_1,y_2, … and making $\Delta' = \Delta/\lambda$ in (29),

$$\left(\frac{\partial f(x_1, x_2, \ldots; \lambda y_1, \lambda y_2, \ldots)}{\partial(\lambda y_1)}\right)_{x_1, x_2, \ldots; \lambda y_2, \lambda y_3, \ldots}$$

$$= \lim_{\Delta' \to 0} \frac{f(x_1, x_2, \ldots; y_1 + \Delta', y_2, \ldots) - f(x_1, x_2, \ldots; y_1, y_2, \ldots)}{\Delta'} = \left(\frac{\partial f(x_1, x_2, \ldots; y_1, y_2, \ldots)}{\partial y_1}\right)_{x_1, x_2, \ldots; y_2, y_3, \ldots} \tag{30}$$

The differential of f with respect to λ in the right side of (24) is:

$$\frac{d[\lambda f(x_1, x_2, \ldots; y_1, y_2, \ldots)]}{d\lambda} = f(x_1, x_2, \ldots; y_1, y_2, \ldots) \tag{31}$$

Eq. (25) is obtained by substituting Eqs. (27), (28), (30), (31) in Eq. (26). In addition, it is interesting to see that, defining f_1 as $f_1 = (\partial f/\partial x_1)$ and using (30), f_1 is a homogeneous function of zero degree with respect to the variables y_1, y_2,…:

$$f_1(x_1, x_2, \ldots; \lambda y_1, \lambda y_2, \ldots) = f_1(x_1, x_2, \ldots; y_1, y_2, \ldots) \tag{32}$$

3. Thermodynamic descriptions

3.1. Description by components

Let it be a three-component system (e.g., as those of **Figure 1A** and **C**). Being J an extensive property, a description by components is:

$$J = J(n_1, n_2, n_3) \tag{33}$$

where n_1, n_2 and n_3 are the number of moles of components 1, 2 and 3. The partial property of 1 is defined as:

$$j_{1;2,3}(n_1, n_2, n_3) = \left(\frac{\partial J(n_1, n_2, n_3)}{\partial n_1}\right)_{n_2, n_3} \tag{34}$$

From the above section, we know that $j_{1;2,3}$ is homogeneous function of zero degree with respect to n_1, n_2 and n_3. With this and considering $\lambda = 1/(n_1+n_2+n_3)$,

$$\begin{aligned} j_{1;2,3}(n_1, n_2, n_3) &= j_{1;2,3}\left(\frac{n_1}{n_1+n_2+n_3}, \frac{n_2}{n_1+n_2+n_3}, \frac{n_3}{n_1+n_2+n_3}\right) = \\ &= j_{1;2,3}(x_1, x_2, x_3) = j_{1;2,3}(x_2, x_3) \end{aligned} \tag{35}$$

where we have considered that x_1 is a function of x_2 and x_3 because $x_1 = 1-x_2-x_3$. From (35), we see that the partial molar properties depend only on the composition of the system. Alternatively to (35), we could use other scales of composition/concentration to express $j_{1;2,3}$.

The equation of Gibbs is obtained by differentiating J in (33) and using Eq. (34) and similar definitions for components 2 and 3:

$$dJ = j_{1;2,3}dn_1 + j_{2;1,3}dn_2 + j_{3;1,2}dn_3 \tag{36}$$

The Euler equation is obtained by considering that J is a homogeneous function with respect to n_1, n_2 and n_3 and applying the Euler's theorem:

$$J = n_1 j_{1;2,3} + n_2 j_{2;1,3} + n_3 j_{3;1,2} \tag{37}$$

The Gibbs-Duhem equation is obtained by differentiating in Eq. (37), equalling to Eq. (36) and cancelling common terms:

$$0 = n_1 dj_{1;2,3} + n_2 dj_{2;1,3} + n_3 dj_{3;1,2} \tag{38}$$

If we consider that partial molar properties are function of n_1, n_2 and n_3, Eq. (38) would be the Gibbs-Duhem equation in the representation of variables n_1, n_2 and n_3. The representation in the variables x_2 and x_3 is as follows. Dividing (38) by the total number of moles,

$$0 = x_1 dj_{1;2,3} + x_2 dj_{2;1,3} + x_3 dj_{3;1,2} \tag{39}$$

Calculating the differentials by considering that partial molar properties depend on x_2 and x_3, and bearing in mind that x_2 and x_3 are independent variables, (38) can be written in an alternative way as:

$$\begin{cases} x_1\left(\frac{\partial j_{1;2,3}}{\partial x_2}\right)_{x_3} + x_2\left(\frac{\partial j_{2;1,3}}{\partial x_2}\right)_{x_3} + x_3\left(\frac{\partial j_{3;1,2}}{\partial x_2}\right)_{x_3} = 0 \\ x_1\left(\frac{\partial j_{1;2,3}}{\partial x_3}\right)_{x_2} + x_2\left(\frac{\partial j_{2;1,3}}{\partial x_3}\right)_{x_2} + x_3\left(\frac{\partial j_{3;1,2}}{\partial x_3}\right)_{x_2} = 0 \end{cases} \tag{40}$$

3.2. Description by fractions

In a description by fractions, we consider the three-component system as composed of a component 1 and a group (or fraction) composed of components 2 and 3. **Figure 1B** shows

the example when two solutes are grouped in a "complex solute", and **Figure 1D** shows the example in which a polymeric particle composed of polar and non-polar groups is considered as a fraction of the system. In this case, the extensive property J is expressed as:

$$J = J(n_1, n_F, x_{f3}) \tag{41}$$

where

$$n_F = n_2 + n_3 \tag{42}$$

$$x_{f3} = \frac{n_3}{n_2 + n_3} \tag{43}$$

The variable n_F is the total number of moles of the fraction F, and x_{f3} is a variable related to its internal composition. The partial molar properties of J in this description are:

$$j_{1;F}(n_1, n_F, x_{f3}) = \left(\frac{\partial J(n_1, n_F, x_{f3})}{\partial n_1}\right)_{n_F, x_{f3}} \tag{44}$$

$$j_{F;1}(n_1, n_F, x_{f3}) = \left(\frac{\partial J(n_1, n_F, x_{f3})}{\partial n_F}\right)_{n_1, x_{f3}} \tag{45}$$

Because J is a homogeneous function of n_1 and n_F, the partial properties $j_{1;F}$ and $j_{F;1}$ will be homogeneous functions of zero degree with respect to the variables n_1 and n_F. In this way and similarly to Eq. (35):

$$j_{1;F}(n_1, n_F, x_{f3}) = j_{1;F}(x_F, x_{f3}) \tag{46}$$

where $x_F = n_F/(n_1+n_F)$. Now, we will see the relation between both descriptions. From (42) and (43), the change of variable of Eq. (8) is in this case:

$$\begin{cases} n_1(n_1, n_F, x_{f3}) = n_1 \\ n_2(n_1, n_F, x_{f3}) = (1 - x_{f3})n_F \\ n_3(n_1, n_F, x_{f3}) = x_{f3}n_F \end{cases} \tag{47}$$

Substituting (47) in (13) and the result in (17), one obtains that:

$$j_{1;F} = j_{1;2,3} \tag{48}$$

$$j_{F;1} = x_{f2}j_{2;1,3} + x_{f3}j_{3;1,2} \tag{49}$$

$$\left(\frac{\partial J}{\partial x_{f3}}\right)_{n_1, n_F} = n_F(j_{3;1,2} - j_{2;1,3}) \tag{50}$$

The equations of Gibbs, Euler and Gibbs-Duhem in this description are as follows. The Gibbs equation is obtained by differentiating in (41) and considering the definitions given in (44) and (45):

$$dJ = j_{1;F}dn_1 + j_{F;1}dn_F + \left(\frac{\partial J}{\partial x_{f3}}\right)_{n_1, n_F} dx_{f3} \tag{51}$$

The Euler equation is obtained by remembering that J is a homogeneous function of degree one of n_1 and n_F and using the Euler's theorem:

$$J = n_1 j_{1;F} + n_F j_{F;1} \tag{52}$$

The Gibbs-Duhem equation in the representation of variables x_F and x_{f3} is obtained by differentiating in (52), equalling to (51) and cancelling common terms, and dividing by the total number of moles:

$$x_1 dj_{1;F} + x_F dj_{F;1} = x_F(j_{3;1,2} - j_{2;1,3})dx_{f3} \tag{53}$$

Considering that $j_{1;F}$ and $j_{F;1}$ are functions of the independent variables x_F and x_{f3}, then (53) will take the form:

$$\begin{cases} x_1\left(\frac{\partial j_{1;F}}{\partial x_F}\right)_{x_{f3}} + x_F\left(\frac{\partial j_{F;1}}{\partial x_F}\right)_{x_{f3}} = 0 \\ x_1\left(\frac{\partial j_{1;F}}{\partial x_{f3}}\right)_{x_F} + x_F\left(\frac{\partial j_{F;1}}{\partial x_{f3}}\right)_{x_F} = x_F(j_{3;1,2} - j_{2;1,3}) \end{cases} \tag{54}$$

Calculating the partial derivative of $j_{F;1}$ with respect to x_{f3} in Eq. (49) and substituting in Eq. (54), we obtain:

$$\begin{cases} x_1\left(\frac{\partial j_{1;F}}{\partial x_F}\right)_{x_{f3}} + x_F\left(\frac{\partial j_{F;1}}{\partial x_F}\right)_{x_{f3}} = 0 \\ x_1\left(\frac{\partial j_{1;F}}{\partial x_{f3}}\right)_{x_F} + x_F\left[x_{f2}\left(\frac{\partial j_{2;1,3}}{\partial x_{f3}}\right)_{x_F} + x_{f3}\left(\frac{\partial j_{3;1,2}}{\partial x_{f3}}\right)_{x_F}\right]_{x_F} = 0 \end{cases} \tag{55}$$

It is interesting to observe that considering constant composition (dx_{f3} = 0) in Eqs. (51)–(53), then the system behaves as a two-component system. This fact cannot be obtained using the description by components.

4. Partial properties in diluted solutions of multicomponent systems

We consider intuitively a diluted solution when the properties of the solution are similar to those of its solvent in pure state. In this section, we will study the thermodynamic behaviour of the partial molar properties in this region of concentrations.

4.1. Thermodynamic concept of interaction between components

In this paragraph, we will define the concept of non-interaction and prove that when applying it to a system, the system behaves as an ideal mixing. From a thermodynamic point of view, the components of a system are not interacting if both following points hold simultaneously.

1. The state of each component in the system, expressed in terms of its partial molar properties, does not vary by changes of composition of the other components. It means each component does not detect the presence of the other components.
2. The formation of the system from its pure components is carried out with any cost of energy, neither for the system nor for the surroundings.

Mathematically, the first point can be written as:

$$\left(\frac{\partial j_{1;2,3}(x_2,x_3)}{\partial x_2}\right)_{x_3} = \left(\frac{\partial j_{1;2,3}(x_2,x_3)}{\partial x_3}\right)_{x_2} = 0 \Leftrightarrow j_{1;2,3} = j_{1;2,3}(x_1) \tag{56}$$

Substituting (56) in (40) and considering also that:

$$\begin{cases} \left(\frac{\partial j_{1;2,3}}{\partial x_2}\right)_{x_3} = \left(\frac{\partial j_{1;2,3}}{\partial x_1}\right)_{x_3}\left(\frac{\partial x_1}{\partial x_2}\right)_{x_3} = -\left(\frac{\partial j_{1;2,3}}{\partial x_1}\right)_{x_3} \\ \left(\frac{\partial j_{1;2,3}}{\partial x_3}\right)_{x_2} = \left(\frac{\partial j_{1;2,3}}{\partial x_1}\right)_{x_2}\left(\frac{\partial x_1}{\partial x_3}\right)_{x_2} = -\left(\frac{\partial j_{1;2,3}}{\partial x_1}\right)_{x_2} \end{cases} \tag{57}$$

it is obtained that:

$$\begin{cases} -x_1\left(\frac{\partial j_{1;2,3}}{\partial x_1}\right)_{x_3} + x_2\left(\frac{\partial j_{2;1,3}}{\partial x_2}\right)_{x_3} = 0 \\ -x_1\left(\frac{\partial j_{1;2,3}}{\partial x_1}\right)_{x_2} + x_3\left(\frac{\partial j_{2;1,3}}{\partial x_3}\right)_{x_2} = 0 \end{cases} \tag{58}$$

Because $j_{1;2,3}$ depends only on x_1:

$$\left(\frac{\partial j_{1;2,3}}{\partial x_1}\right)_{x_2} = \left(\frac{\partial j_{1;2,3}}{\partial x_1}\right)_{x_3} \tag{59}$$

and then (57) yields:

$$x_1\left(\frac{\partial j_{1;2,3}(x_1)}{\partial x_1}\right)_{x_3} = x_2\left(\frac{\partial j_{2;1,3}(x_2)}{\partial x_2}\right)_{x_3} = x_3\left(\frac{\partial j_{3;1,2}(x_3)}{\partial x_3}\right)_{x_3} \tag{60}$$

Because the first term depends only on x_1 and the second and third terms depend only on x_2 and x_3, respectively, from (60), we have that:

$$x_1\frac{dj_{1;2,3}}{dx_1} = k_J(T,P) \tag{61}$$

where k_J is a function, which only depends on temperature T and pressure P. Similar equations to (61) are obtained for $j_{2;1,3}$ and $j_{3;1,2}$. Integrating in (61) between $x'_1 = 1$ and x_1,

$$j_{1;2,3}(x_1) = j_1 + k_J(T,P)\ln(x_1) \tag{62}$$

For components 2 and 3, similar equations to (62) are obtained. Now, we will apply the second point of the above definition of non-interaction. The zero cost of energy for the system and surroundings is equivalent to:

$$Q_{mix} = W_{mix} = 0 \Rightarrow \Delta U_{mix} = 0 \Rightarrow \begin{cases} u_{1;2,3} = u_1 \\ h_{1;2,3} = h_1 \\ v_{1;2,3} = v_1 \end{cases} \tag{63}$$

Considering $u_{1;\,2,3}$, $h_{1;\,2,3}$ and $v_{1;\,2,3}$ as (62) and bearing in mind (63):

$$k_U(T,P) = k_H(T,P) = k_V(T,P) = 0 \tag{64}$$

In addition to this $g_{1;2,3}$ (free energy of Gibbs),

$$v_{1;2,3} = \left(\frac{\partial g_{1;2,3}}{\partial P}\right)_{T,x_2,x_3} \Rightarrow k_V(T,P) = \left(\frac{\partial k_G(T,P)}{\partial P}\right)_T \tag{65}$$

$$\frac{h_{1;2,3}}{T^2} = -\left(\frac{\partial}{\partial T}\left(\frac{g_{1;2,3}}{T}\right)\right)_{P,x_2,x_3} \Rightarrow \frac{k_H(T,P)}{T^2} = -\left(\frac{\partial}{\partial T}\left(\frac{k_G(T,P)}{T}\right)\right)_T \tag{66}$$

Combining Eqs. (64)–(66), we have that:

$$k_G(T,P) = kT \tag{67}$$

where k is a constant. For the entropy, one gets:

$$-s_{1;2,3} = \left(\frac{\partial g_{1;2,3}}{\partial T}\right)_{P,x_2,x_3} \Rightarrow -k_S(T,P) = \left(\frac{\partial k_G(T,P)}{\partial T}\right)_P \tag{68}$$

With this,

$$g_{1;2,3} = g_1 + kT\ln(x_1) \tag{69}$$

$$s_{1;2,3} = s_1 - k\ln(x_1) \tag{70}$$

and we have demonstrated that a system holding the non-interaction definition proposed is an ideal mixing.

4.2. Diluted solutions

In this section, we will define the thermodynamic concept of diluted solutions and study the behaviour of the partial molar properties of these solutions. Commonly and intuitively, we consider a solution as diluted when its properties are similar to those of the pure solvent. We can implement mathematically this concept in the following way. When we remove all solutes from a solution, we have that:

$$\lim_{x_2+x_3\to 0} j(x_2,x_3) = j_1 \tag{71}$$

where j is the molar property of the extensive thermodynamic property J. In addition, the partial derivatives must vanish:

$$\lim_{x_2+x_3\to 0}\left(\frac{\partial j_{1;2,3}(x_2,x_3)}{\partial x_2}\right)_{x_3}=\lim_{x_2+x_3\to 0}\left(\frac{\partial j_{1;2,3}(x_2,x_3)}{\partial x_3}\right)_{x_2}=0 \tag{72}$$

Otherwise, we would have memory effects and we can see this with an example. If we purify water, the pure substance obtained does not depend on the initial diluted solution employed. Actually, pure water is commonly used as a standard because it does not depend on the part of world, in which it is obtained. The Taylor's expansion of $j_{1;2,3}$ is:

$$j_{1;2,3}(x_2,x_3)=j_1(0,0)+[\nabla j_{1;2,3}(0,0)]^{\mathrm{T}}\begin{bmatrix}x_2\\x_3\end{bmatrix}+\frac{1}{2}(x_2,x_3)\mathbf{H}j_{1;2,3}(0,0)\begin{bmatrix}x_2\\x_3\end{bmatrix}+\ldots \tag{73}$$

where $\nabla j_{1;2,3}(0,0)$ and $\mathbf{H}j_{1;2,3}(0,0)$ are, respectively, the vector gradient and the Hessian of $j_{1;2,3}$ matrix at (0,0). Considering (71) and (72) in (73) and that all partial derivatives mush vanish at (0,0), we have that for diluted solutions:

$$j_{1;2,3}(x_2,x_3)\approx j_1+\ldots \tag{74}$$

From Eq. (74), we have for diluted solutions:

$$\left(\frac{\partial j_{1;2,3}}{\partial x_2}\right)_{x_3}\approx\left(\frac{\partial j_{1;2,3}}{\partial x_3}\right)_{x_2}\approx 0 \tag{75}$$

The behaviour of molar partial properties of solutes is as follows. Considering a "complex solute" S composed of 2 and 3 (as in **Figure 1B**),

$$j_{1;S}(x_S,x_{s3})\approx j_1 \tag{76}$$

and substituting Eq. (74) in the first equation of (55),

$$\left(\frac{\partial j_{S;1}}{\partial x_S}\right)_{x_{s3}}\approx 0\Leftrightarrow j_{S;1}(x_S,x_{s3})\approx j_{S;1}(x_{s3}) \tag{77}$$

Inserting Eq. (76) in the second equation of (55), it is obtained that:

$$x_{s2}\left(\frac{\partial j_{2;1,3}}{\partial x_{s3}}\right)_{x_S}+x_{s3}\left(\frac{\partial j_{3;1,2}}{\partial x_{s3}}\right)_{x_S}\approx 0 \tag{78}$$

Until now, we have seen the effect of the dilution in the capacity of detecting the presence of other components in a diluted solution. In order to gain an insight into the interactions, we have to study the process of mixing in diluted solutions. From (71), we can write:

$$\begin{cases}\lim_{x_2+x_3\to 0}\ h=h_1\Rightarrow\lim_{x_2+x_3\to 0}\ q_{mix}=\lim_{x_2+x_3\to 0}\ \Delta_{mix}h=0\\ \lim_{x_2+x_3\to 0}\ v=v_1\Rightarrow\lim_{x_2+x_3\to 0}\ w_{mix}=\lim_{x_2+x_3\to 0}-P\Delta_{mix}v=0\end{cases} \tag{79}$$

It indicates that in the limit of infinite dilution, components do not interact because the process of mixture does not have any energy cost. This result implicates that in diluted solutions, according to the asymptotic approach given by Eq. (74), the interaction between solvent and solutes is weak and it can be neglected.

4.3. Partial molar properties of interaction in diluted solutions

The molar property j of a diluted solution can be written as:

$$j \approx x_1 j_1 + x_S j_{S;1} \tag{80}$$

where we are considering the interaction between components 2 and 3 since

$$j_{S;1} = x_{s2} j_{2;1,3} + x_{s3} j_{3;1,2} \tag{81}$$

In a diluted solution without interaction between 2 and 3, the property $j^{\varnothing}$ can be written as:

$$j^{\varnothing} = x_1 j_1 + x_S (x_{s2} j_{2;1} + x_{s3} j_{3;1}) \tag{82}$$

In this way, we can calculate the interaction contributions to j as:

$$\Delta j^{\text{int}} = j - j^{\varnothing} \approx x_S \Delta j_{S;1} \tag{83}$$

where

$$\Delta j_{S;1} = x_{s2} \Delta j_{2;1,3} + x_{s3} \Delta j_{3;1,2} \tag{84}$$

is the partial molar property of interaction of the complex solute and

$$\begin{cases} \Delta j_{2;1,3} = j_{2;1,3} - j_{2;1} \\ \Delta j_{3;1,2} = j_{3;1,2} - j_{3;1} \end{cases} \tag{85}$$

are the partial molar properties of interaction of the components 2 and 3, respectively. These properties are not independent as we will see as follows. Combining (78) and (85),

$$x_{s2} \left(\frac{\partial \Delta j_{2;1,3}}{\partial x_{s3}} \right)_{x_S} + x_{s3} \left(\frac{\partial \Delta j_{3;1,2}}{\partial x_{s3}} \right)_{x_S} + x_{s2} \left(\frac{\partial j_{2;1}}{\partial x_{s3}} \right)_{x_S} + x_{s3} \left(\frac{\partial j_{3;1}}{\partial x_{s3}} \right)_{x_S} \approx 0 \tag{86}$$

In Eq. (85), $\Delta j_{2;1,3}$ and $\Delta j_{3;1,2}$ are evaluated when using concentrations x_S and x_{s3}. Accordingly, $j_{2,1}$ is evaluated using the concentration x_2 given by $x_2 = x_S\,(1 - x_{s3})$, and then,

$$\left(\frac{\partial j_{2;1}}{\partial x_{s3}} \right)_{x_S} = \frac{dj_{2;1}}{dx_2} \left(\frac{\partial x_2}{\partial x_{s3}} \right)_{x_S} = -x_S \frac{dj_{2;1}}{dx_2} \tag{87}$$

Considering the Gibbs-Duhem equation for a two-component system:

$$x_1 \frac{dj_{1;2}}{dx_2} + x_2 \frac{dj_{2;1}}{dx_2} = 0 \tag{88}$$

in Eq. (87) and bearing in mind that solutions are diluted,

$$x_{s2}\left(\frac{\partial j_{2;1}}{\partial x_{s3}}\right)_{x_S} = x_1 \frac{dj_{1;2}}{dx_2} \approx 0 \tag{89}$$

Similarly for component 3,

$$x_{s3}\left(\frac{\partial j_{3;1}}{\partial x_{s3}}\right)_{x_S} = x_1 \frac{dj_{1;3}}{dx_3} \approx 0 \tag{90}$$

Substituting (89) and (90) in (86), we obtain:

$$x_{s2}\left(\frac{\partial \Delta j_{2;1,3}}{\partial x_{s3}}\right)_{x_S} + x_{s3}\left(\frac{\partial \Delta j_{3;1,2}}{\partial x_{s3}}\right)_{x_S} \approx 0 \tag{91}$$

Eq. (91) indicates that in a diluted solution, the interaction between components 2 and 3 is not vanished. The partial molar property of interaction of the complex solute can be calculated experimentally as:

$$\Delta j_{S;1} \approx j_{S;1} - (x_{s2} j_{2;1} + x_{s3} j_{3;1}) \tag{92}$$

and the partial properties of interaction of components 2 and 3 can be obtained from (92) using the equations:

$$\begin{cases} \Delta j_{2;1,3} \approx \Delta j_{S;1} - x_{s3} \dfrac{d\Delta j_{S;1}}{dx_{s3}} \\ \Delta j_{3;1,2} \approx \Delta j_{S;1} + (1 - x_{s3}) \dfrac{d\Delta j_{S;1}}{dx_{s3}} \end{cases} \tag{93}$$

Eq. (93) is obtained by differentiating in Eq. (92) with respect to x_{s3}, using Eq. (91) and combining the result with Eq. (92). As we will see below, Eq. (93) will allow us to obtain the interaction partial properties of 2 and 3 from experimental data.

4.4. Experimental determination of partial molar properties of interaction in diluted solutions

4.4.1. Partial specific volumes of interaction and partial specific adiabatic compressibility of interaction

As an example, we will consider the interaction between functionalized polymeric particles and an electrolyte at 30°C [4]. For that, polymeric particles synthesized of poly(n-butyl acrylate-co-methyl methacrylate) functionalized with different concentrations of acrylic acid were used in this study. The electrolyte was NaOH. Similarly to **Figure 1A**, water (solvent) was considered as component 1, polymeric particles as component 2 and electrolyte as component

3. And similarly to **Figure 1B**, the system was fractionalized in component 1 and a complex solute composed of polymeric particles and electrolyte. The experimental measurements were carried out using a Density and Sound Analyzer DSA 5000 from Anton-Paar connected to a titration cell. It is of full cell type, which is usually employed in isothermal titration calorimetry. Polymeric particles were located in the titration cell, and electrolyte was located in the syringe. Concentrations of polymeric particles (c_2) and electrolyte (c_3) after each titration were calculated as [4, 5]:

$$\begin{cases} c_2^{i+1} = c_2^i \, e^{-\frac{v}{V}} \\ c_3^{i+1} = c_3^s - (c_3^s - c_3^i) \, e^{-\frac{v}{V}} \end{cases} \tag{94}$$

where V is the effective volume of the titration cell, v is the titration volume and c_3^s is the stock concentration of electrolyte in the syringe. **Figure 3A** and **B** shows, respectively, data of density (ρ) and sound speed (u) as function of the electrolyte concentration. The specific volume (v) and the specific adiabatic compressibility (ks) were calculated as:

$$v = \frac{1}{\rho} \tag{95}$$

$$k_s = \left(\frac{10}{\rho u}\right)^2 \tag{96}$$

Considering the solution in the cell as diluted, the partial specific volume (and similarly the partial specific adiabatic compressibility) of the complex solute can be calculated as:

$$v_{S;1} = \frac{v - t_1 v_1}{t_S} \tag{97}$$

where t_1 and t_S are the mass fraction of the water and of the complex solute, respectively. **Figure 3C** and **D** shows the partial specific volume and partial specific adiabatic compressibility as function of t_{f3} (mass fraction of the electrolyte in the complex solute). The term of interaction $\Delta v_{S;1}$ is calculated by Eq. (92), where $v_{2;1}$ is obtained by considering that:

$$v_{2;1} = \lim_{t_{s3} \to 0} v_{S;1} \tag{98}$$

in **Figure 3C**. The term $v_{3;1}$ is calculated by extrapolating the linear part of $v_{S;1}$ in **Figure 3C** as:

$$v_{3;1} = \lim_{t_{s3} \to 1} v_{S;1} \tag{99}$$

The partial specific volume of interaction of the polymeric particles ($\Delta v_{2;1,3}$) and the partial specific volume of interaction of the electrolyte ($\Delta v_{3;1,2}$) were obtained using Eq. (93). The numerical method employed to calculate the derivatives is shown elsewhere [4]. **Figure 4** shows the values of $\Delta v_{S;1}$, $\Delta v_{2;1,3}$ and $\Delta v_{3;1,2}$, and **Figure 5** shows the values of $\Delta k_{s\ S;1}$, $\Delta k_{s\ 2;1,3}$ and $\Delta k_{s\ 3;1,2}$ obtained in a similar way than for volumes.

Partial volume of polymeric particles ($v_{2;1}$) can be broken down in the following contributions [6–11]:

$$v_{2;1} = v_{2;1/atom} + v_{2;1/free} + v_{2;1/hyd} \tag{100}$$

which are shown in **Figure 6**. The atomic volume contribution ($v_{2;1/atom}$) is the sum of all volumes of the atoms, which make up polymeric chains. The free volume contribution ($v_{2;1/free}$) is consequence of the imperfect packing of the polymeric chains. The atomic volume contribution and free volume contribution are both positive contributions. The hydration contribution ($v_{2;1/hyd}$) is negative, as a consequence of that the specific volume of water molecules in bulk is larger than the specific volume in the hydration shell. The contributions to the partial specific adiabatic compressibility are the free volume and hydration because the effect of the pressure on the atomic volume is neglected [10, 12–21]:

$$k_{T\,2;1} = -\left(\frac{\partial v_{2;1}}{\partial P}\right)_T = -\left(\frac{\partial v_{2;1/free}}{\partial P}\right)_T - \left(\frac{\partial v_{2;1/hyd}}{\partial P}\right)_T = k_{T\,2;1/free} + k_{T\,2;1/hyd} \tag{101}$$

The contribution $k_{T\,2;1/free}$ is positive, and the contribution $k_{T\,2;1/hyd}$ is negative [4, 8]. In this chapter, we will take the adiabatic compressibility as an approximation of the isothermal

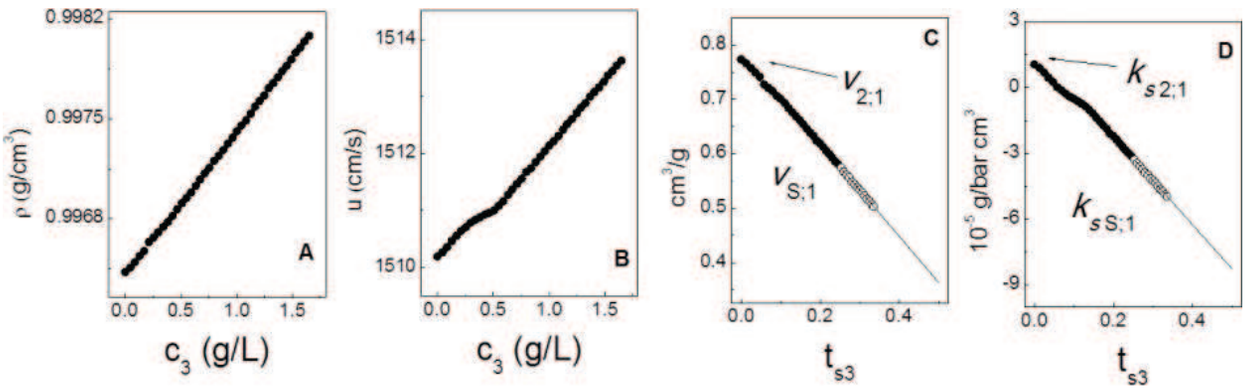

Figure 3. (A) Density as function of the electrolyte concentration c_3 (g/L). (B) Sound speed as function of the electrolyte concentration. (C) Partial specific volume of the complex solute composed of polymeric particles and electrolyte as function of the mass fraction of the electrolyte in the complex solute (t_{s3}). (D) Partial specific adiabatic compressibility of the complex solute as function of t_{f3}.

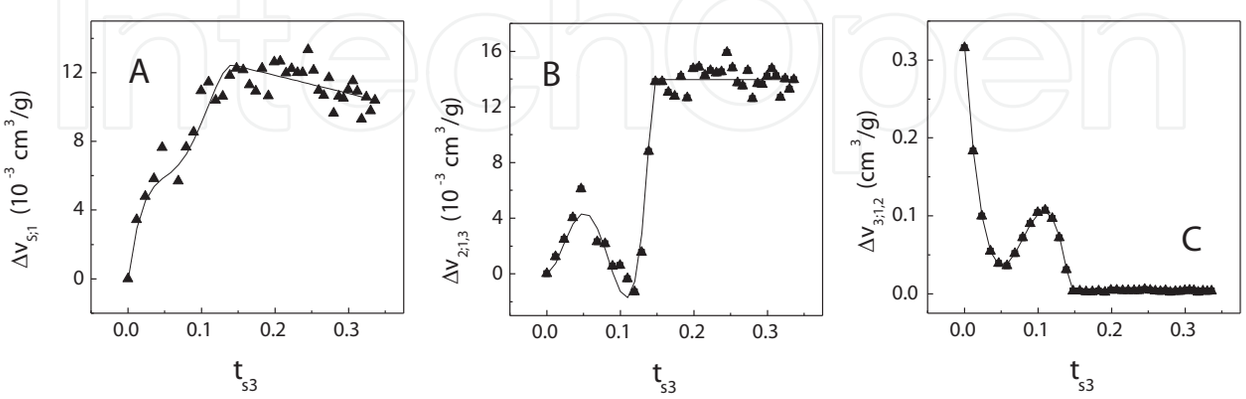

Figure 4. (A) Partial specific volume of interaction of the complex solute (polymeric particles + electrolyte) as function of the mass fraction of the electrolyte in the complex solute (t_{s3}). (B) Partial specific volume of interaction of the polymeric particles as function of t_{s3}. (C) Partial specific volume of interaction of the electrolyte as function of t_{s3}.

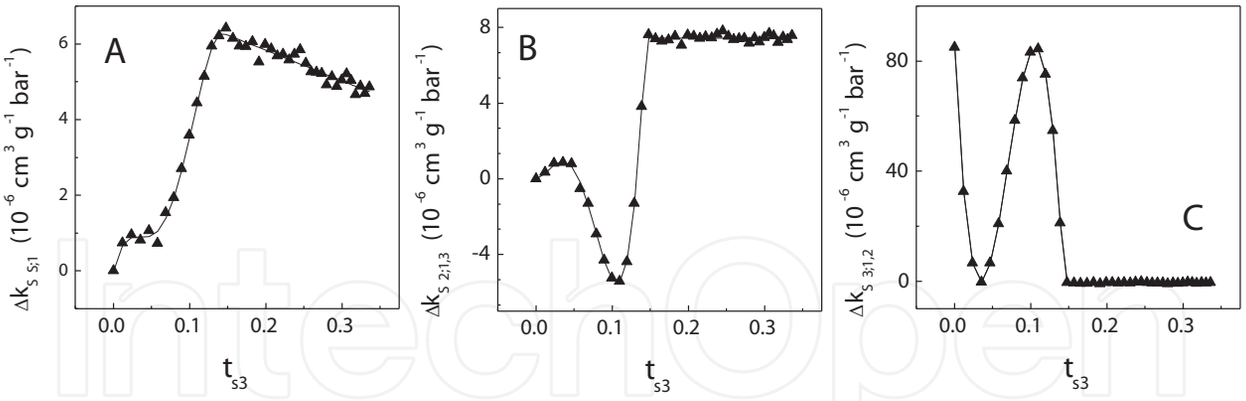

Figure 5. (A) Partial specific adiabatic compressibility of interaction of the complex solute (polymeric particles + electrolyte) as function of the mass fraction of the electrolyte in the complex solute (t_{s3}). (B) Partial specific adiabatic compressibility of interaction of the polymeric particles as function of t_{s3}. (C) Partial specific adiabatic compressibility of interaction of the electrolyte as function of t_{s3}.

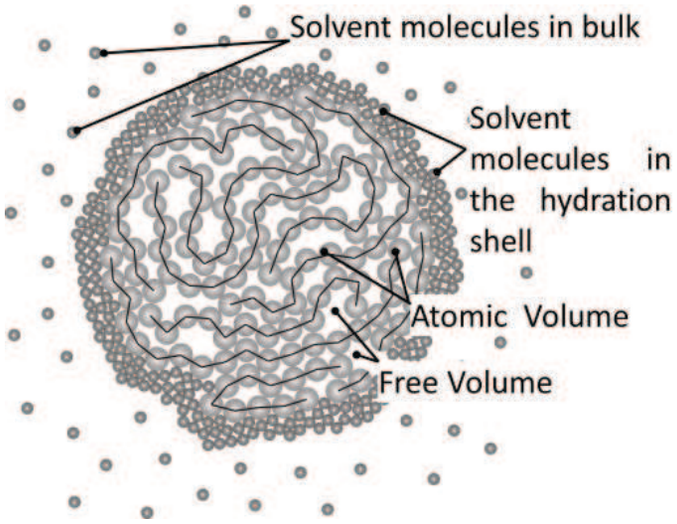

Figure 6. Contributions to the partial volume in a polymeric particle.

compressibility. For the electrolyte, the free volume contribution is null, and then, $v_{3;1}$ and $k_{T\,3;1}$ will take the following form:

$$v_{3;1} = v_{3;1/atom} + v_{3;1/hyd} \tag{102}$$

$$k_{T3;1} = -\left(\frac{\partial v_{3;1}}{\partial P}\right)_T = -\left(\frac{\partial v_{3;1/hyd}}{\partial P}\right)_T = k_{T3;1/hyd} \tag{103}$$

For the complex solute, we can write a similar breakdown:

$$v_{S;1} = v_{S;1/atom} + v_{S;1/free} + v_{S;1/hyd} \tag{104}$$

Inserting Eqs. (100), (102) and (104) in Eq. (92) and neglecting the variation in the atomic contributions, the following equation for the interaction specific partial volume is obtained:

$$\Delta v_{S,1} = \Delta v_{S,1/free} + \Delta v_{S,1/hyd} \tag{105}$$

where

$$\Delta v_{S;1/free} = v_{S;1/free} - t_{s2} v_{2;1/free} \tag{106}$$

$$\Delta v_{S;1/hyd} = v_{S;1/hyd} - (t_{s2} v_{2;1/hyd} + t_{s3} v_{3;1/hyd}) \tag{107}$$

Substituting (105) in (93), we get

$$\begin{cases} \Delta v_{2;1,3} = \left(\Delta v_{S;1/free} - t_{s3} \dfrac{d\Delta v_{S;1/free}}{dt_{s3}}\right) + \left(\Delta v_{S;1/hyd} - t_{s3} \dfrac{d\Delta v_{S;1/hyd}}{dt_{s3}}\right) \\ \Delta v_{3;1,2} = \left(\Delta v_{S;1/free} + (1 - t_{s3}) \dfrac{d\Delta v_{S;1/free}}{dt_{s3}}\right) + \left(\Delta v_{S;1/hyd} + (1 - t_{s3}) \dfrac{d\Delta v_{S;1/hyd}}{dt_{s3}}\right) \end{cases} \tag{108}$$

Defining now:

$$\begin{aligned} \Delta v_{2;1,3/free} &= \Delta v_{S;1/free} - t_{s3} \frac{d\Delta v_{S;1/free}}{dt_{s3}} \\ \Delta v_{2;1,3/hyd} &= \Delta v_{S;1/hyd} - t_{s3} \frac{d\Delta v_{S;1/hyd}}{dt_{s3}} \\ \Delta v_{3;1,2/free} &= \Delta v_{S;1/free} + (1 - t_{s3}) \frac{d\Delta v_{S;1/free}}{dt_{s3}} \\ \Delta v_{3;1,2/hyd} &= \Delta v_{S;1/hyd} + (1 - t_{s3}) \frac{d\Delta v_{S;1/hyd}}{dt_{s3}} \end{aligned} \tag{109}$$

One arrives at the following result:

$$\begin{aligned} \Delta v_{2;1,3} &= \Delta v_{2;1,3/free} + \Delta v_{S;1/free} \\ \Delta v_{3;1,2} &= \Delta v_{3;1,2/free} + \Delta v_{3;1,2/hyd} \end{aligned} \tag{110}$$

where similar equations are obtained for the interaction partial specific compressibilities.

Considering these contributions, the interpretation of the partial specific volumes of interaction of the particle as function of the electrolyte concentration is as follows. From t_{f3} = 0 to around 0.05 (see **Figure 4B**), there is an increment in $\Delta v_{2,1,3}$ which can be interpreted as a gain of free volume by the disentanglement of the polymeric chains. This increment of free volume is accompanied by an increment in the hydrodynamic radius [4]. From around t_{f3} = 0.05 to around 0.1, there is a decrement in $\Delta v_{2,1,3}$ due to hydration. In this region of compositions, the separation of polymeric chains allows the entrance of water molecules in the polymeric particle. As a result, the hydrodynamic radius of the particle increases [4]. From around t_{s3} = 0.1 to 0.15, $\Delta v_{2,1,3}$ increases sharply. This fact can be interpreted as an increment of the dehydration. Beyond t_{s3} = 0.15, $\Delta v_{2,1,3}$ becomes constant, indicating that the interaction between particles and the

electrolyte is saturated. Similar regions with similar interpretations are obtained for the partial specific adiabatic compressibility (see **Figure 5B**).

4.4.2. Partial specific enthalpies of interaction

This section deals with the determination of the partial specific enthalpies of interaction of the same system than in the latest example [4]. Partial specific enthalpy of interaction of polymeric particles is:

$$\Delta h_{2;1,3} = h_{2;1,3} - h_{2;1} \tag{111}$$

and the partial specific enthalpy interaction of the electrolyte is:

$$\Delta h_{3;1,2} = h_{3;1,2} - h_{3;1} \tag{112}$$

The partial specific enthalpy of interaction of the electrolyte can be measured by isothermal titration calorimetry using the combination of two experiments [6, 7]. The first experiment is locating the polymeric particles in the cell and the electrolyte in the syringe. The heat per unit of titration volume in an infinitesimal titration is:

$$\frac{dQ^{cd}}{dv} = (\rho^s - c_3^s)h_{1;2,3} + c_3^s h_{3;1,2} - h_v(c_3^s) \tag{113}$$

where ρ^s is the density of the stock solution and $h_v(c_3^s)$ is the enthalpy of the stock solution per unit volume. The second experiment consists of titrating water with the above stock solution, and its heat per unit of titration volume in an infinitesimal titration is:

$$\frac{dQ^{c}}{dv} = (\rho^s - c_3^s)h_{1;3} + c_3^s h_{1;3} - h_v(c_3^s) \tag{114}$$

The partial specific enthalpy of interaction of the electrolyte is obtained by subtracting (114) from (113), considering Eq. (112), diluted solutions and bearing in mind that $dn_3^2 = c_3^s dv$:

$$\frac{dQ^{cd}}{dn_3^s} - \frac{dQ^{c}}{dn_3^s} = \Delta h_{3;1,2} \tag{115}$$

Figure 7A shows the experimental values $\Delta h_{3;1,2}$. The partial specific enthalpy of interaction of polymeric particles was calculated by integrating Eq. (91) [7]:

$$\Delta h_{2;1,3}(t_{f3}) = -\int_0^{t_{f3}} \frac{t'_{f3}}{1 - t'_{f3}} \left(\frac{d\Delta h_{3;1,2}}{dt'_{f3}}\right) dt'_{f3} \tag{116}$$

and the values of $\Delta h_{2;1,3}$ are shown in **Figure 7B**. It is very interesting to observe in **Figure 7B** that $\Delta h_{2;1,3}$ is zero from $t_{s3} = 0$ to around $t_{s3} = 0.1$. This fact indicates that the changes, which take place in the first two regions in **Figures 4B** and **5B**, are entropic in origin.

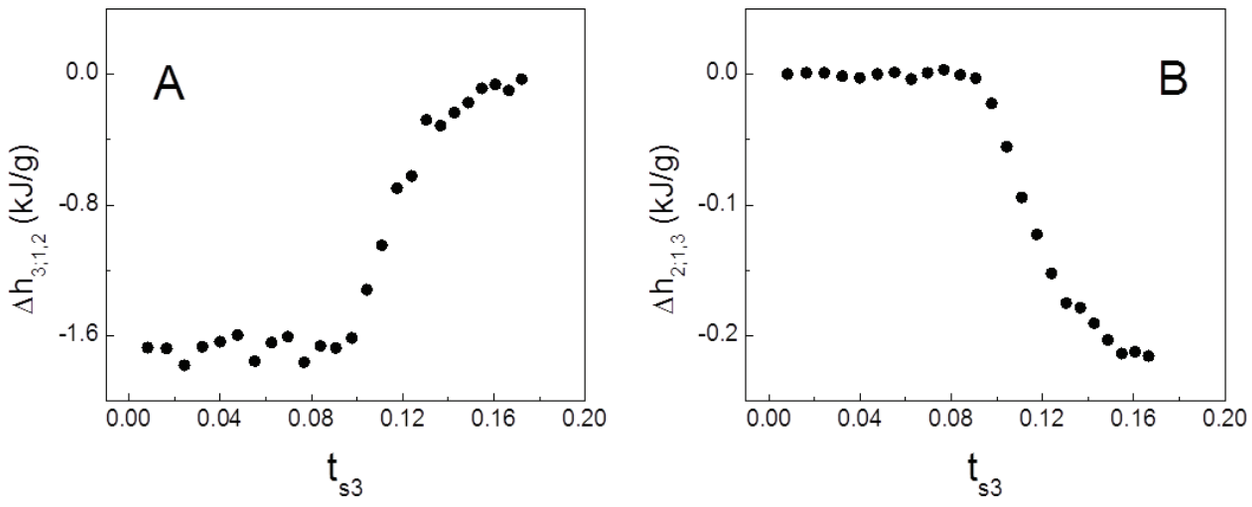

Figure 7. (A) Partial specific enthalpy of interaction of the electrolyte as function of the mass fraction of the electrolyte in the complex solute (t_{s3}). (B) Partial specific enthalpy of interaction of the polymeric particles as function of t_{s3}.

5. Partial molar properties at infinite dilution

First, we will discuss the case of the two-component system and then make the extension to three-component system. In this section, J can be U, H, V or their derivatives $Cv = (\partial H/\partial T)_V$, $C_p = (\partial H/\partial T)_P$ or $E = (\partial V/\partial T)_P$, $K_T = (\partial V/\partial P)_T$ and $K_S = (\partial V/\partial P)_S$.

5.1. Two-component systems

In a two-component system, we only have one way to calculate limits at infinite dilution and it is to take a component as solvent (component 1) and the other as solute (component 2). For a two-component system, j takes the form:

$$j(x_2) = x_1 j_{1;2}(x_2) + x_2 j_{2;1}(x_2) \tag{117}$$

Because

$$\lim_{x_2 \to 0} j(x_2) = j_1 \tag{118}$$

and using Eq. (117), we have:

$$\lim_{x_2 \to 0} j_{1;2}(x_2) = j_1 \tag{119}$$

For the solute, we have:

$$\lim_{x_2 \to 0} j_{2;1}(x_2) = j^o_{2;1} \tag{120}$$

We can obtain experimentally the value of $j^o_{2;1}$ as follows. The Taylor's expansion of $j(x_2)$ around $x_2 = 0$ is:

$$j(x_2) = j(0) + \frac{dj(0)}{dx_2}x_2 + \ldots \tag{121}$$

Differentiating (117) with respect to x_2, considering the Gibbs-Duhem equation for a 2-component system and combining the results with equations (117), (120) and (121):

$$j(x_2) = j_1 + (j^o_{2;1} - j_1)x_2 \tag{122}$$

For this reason, we can obtain experimentally $j^o_{2;1}$ from a linear fit in a plot of $j(x_2)$ as function of x_2.

5.2. Three-component systems

In three-component systems, we have two ways to calculate limits at infinite dilution. The first way is to group two components in a "complex solvent" and to calculate the limit at infinite dilution of the other component in this complex solvent (type I). The other way is considering a component as solvent, to group the other two components in a complex solute, and to calculate the limit at infinite dilution of the complex solute in the solvent (type II).

5.2.1. Limits of type I

In this case, we consider a complex solvent B composed of components 1 and 2 and a solute (component 3). For this system,

$$J = J(n_3, n_B, x_{b2}) \tag{123}$$

where $n_B = n_1 + n_2$ and $x_{b2} = n_2/(n_1+n_2)$. With this, j can be written as:

$$j(x_3, x_{b2}) = x_B j_{B;3}(x_3, x_{b2}) + x_3 j_{3;B}(x_3, x_{b2}) \tag{124}$$

where x_3 is the mole fraction of the component 3. At infinite dilution, we have:

$$\lim_{\substack{x_3 \to 0 \\ x_{b2}\ \text{constant}}} j(x_3, x_{b2}) = j_B(x_{b2}) \tag{125}$$

and then combining Eq. (124) with (125), one gets for the solvent:

$$\lim_{\substack{x_3 \to 0 \\ x_{b2}\ \text{constant}}} j_{B;3}(x_3, x_{b2}) = j_B(x_{b2}) \tag{126}$$

For the solute, it is obtained that:

$$\lim_{\substack{x_3 \to 0 \\ x_{b2}\ \text{constant}}} j_{3;B}(x_3, x_{b2}) = j^o_{3;B}(x_{b2}) \equiv j^o_{3;1,2}(x_{b2}) \tag{127}$$

where we have used Eq. (48). Similarly to the case of two-component systems, the amount $j^o_{3;1,2}$ can be obtained experimentally by using the equation:

$$j(x_3, x_{b2}) = j_B(x_{b2}) + \left(j^o_{3;1,2} - j_B(x_{b2})\right)x_3 \tag{128}$$

This equation is obtained by using the first-order Taylor's expansion of $j(x_3,x_{b2})$ around $x_3 = 0$, the partial derivative of $j(x_3, x_{b2})$ with respect to x_3, the Gibbs-Duhem equation of the fractionalized system considering the composition of the fraction as constant and Eqs. (126) and (127).

5.2.2. Limits of type II

In this case (see **Figure 1A** and **B**), we will consider the component 1 as solvent and a "complex solute" S composed of 2 and 3 and then:

$$J = J(n_1, n_S, x_{s3}) \tag{129}$$

where $n_S = n_2+n_3$ and $x_{s3} = n_3/(n_2 + n_3)$. The molar property j is:

$$j(x_S, x_{s3}) = x_1 j_{1;S}(x_S, x_{s3}) + x_S j_{S;1}(x_S, x_{s3}) \tag{130}$$

Similarly to the above cases, at infinite dilution we have for the solvent:

$$\lim_{\substack{x_S \to 0 \\ x_{s3}\ \text{constant}}} j_{1;S}(x_S, x_{s3}) = j_1 \tag{131}$$

Accordingly to case of the two-component system, one gets for the complex solute:

$$\lim_{\substack{x_S \to 0 \\ x_{s3}\ \text{constant}}} j_{S;1}(x_S, x_{s3}) = j^o_{S;1}(x_{s3}) \tag{132}$$

and in a similar way than for the type I limits, $j^o_{S;1}$ can be calculated as

$$j(x_S, x_{s3}) = j_1 + \left(j^o_{S;1}(x_{s3}) - j_1\right) x_S \tag{133}$$

In order to study the contributions of components 2 and 3 to $j^o_{S;1}$, we define the following limits an infinite dilution:

$$\begin{cases} \lim_{\substack{x_S \to 0 \\ x_{s3}\ \text{constant}}} j_{2;1,3}(x_S, x_{s3}) = j^{\Delta}_{2;1,3}(x_{s3}) \\ \lim_{\substack{x_S \to 0 \\ x_{s3}\ \text{constant}}} j_{3;1,2}(x_S, x_{s3}) = j^{\Delta}_{3;1,2}(x_{s3}) \end{cases} \tag{134}$$

In this way, taking limits in both sides of Eq. (49), and bearing in mind Eqs. (132) and (134), we have that:

$$j^o_{S;1}(x_{s3}) = x_{s2} j^{\Delta}_{2;1,3}(x_{s3}) + x_{s3} j^{\Delta}_{3;1,2}(x_{s3}) \tag{135}$$

Now, we will see some mathematical properties of limits of type II. One of them is for example:

$$\lim_{x_{s3} \to 0} j^{\Delta}_{2;1,3}(x_{s3}) = j^o_{2;1} \tag{136}$$

This property is demonstrated by using iterated limits:

$$\lim_{x_{s3}\to 0} j^{\Delta}_{2;1,3}(x_{s3}) = \lim_{\substack{x_{s3}\to 0 \\ x_S \text{ constant}}} \left[\lim_{\substack{x_S \to 0 \\ x_{s3} \text{ constant}}} j_{2;1,3}(x_S, x_{s3}) \right]$$

$$= \lim_{\substack{x_S \to 0 \\ x_{s3} \text{ constant}}} \left[\lim_{\substack{x_{s3}\to 0 \\ x_S \text{ constant}}} j_{2;1,3}(x_S, x_{s3}) \right] = \lim_{x_S\to 0} j_{2;1,3}(x_S, 0) = \lim_{x_2\to 0} j_{2;1}(x_2) = j^{o}_{2;1} \tag{137}$$

The other mathematical property is:

$$\lim_{x_{s3}\to 1} j^{\Delta}_{3;1,2}(x_{s3}) = j^{o}_{2;1,3}(0) \tag{138}$$

where its demonstration is as follows:

$$\lim_{x_{s3}\to 1} j^{\Delta}_{3;1,2}(x_{s3}) = \lim_{\substack{x_{s3}\to 1 \\ x_S \text{ constant}}} \left[\lim_{\substack{x_S \to 0 \\ x_{s3} \text{ constant}}} j_{3;1,2}(x_S, x_{s3}) \right]$$

$$= \lim_{\substack{x_S \to 0 \\ x_{s3} \text{ constant}}} \left[\lim_{\substack{x_{s3}\to 1 \\ x_S \text{ constant}}} j_{3;1,2}(x_S, x_{s3}) \right] \tag{139}$$

Now, it is necessary to consider other way to fractionalize the system. For convenience, we will consider a complex solvent B composed of 1 and 3, and a solute 2 where the variable x_B represents the molar fraction of B and $x_{b3} = n_3/(n_1+n_3)$. With this,

$$\begin{cases} \lim\limits_{\substack{x_{s3}\to 1 \\ x_S \text{ constant}}} x_2 = \lim\limits_{\substack{x_{s3}\to 1 \\ x_S \text{ constant}}} x_S(1 - x_{s3}) = 0 \\ \lim\limits_{\substack{x_{s3}\to 1 \\ x_S \text{ constant}}} x_{b3} = \lim\limits_{\substack{x_{s3}\to 1 \\ x_S \text{ constant}}} x_{s3}x_S[1 - x_S(1 - x_{s3})] = x_S \end{cases} \tag{140}$$

and considering Eq. (140), (139) transforms into:

$$\lim_{x_{s3}\to 1} j^{\Delta}_{3;1,2}(x_{s3}) = \lim_{\substack{x_S \to 0 \\ x_{s3} \text{ constant}}} \left[\lim_{\substack{x_2 \to 0 \\ x_{b2} \text{ constant}}} j_{3;1,2}(x_2, x_{b2}) \right] = \lim_{\substack{x_S \to 0 \\ x_{s3} \text{ constant}}} j^{o}_{3;1,2}(x_{b2}) = j^{o}_{3;1,2}(0) \tag{141}$$

Other interesting property of the limits of type II is that they are related to each other by the following equation:

$$x_{s2}\frac{dj^{\Delta}_{2;1,3}}{dx_{s3}} + x_{s3}\frac{dj^{\Delta}_{3;1,2}}{dx_{s3}} = 0 \tag{142}$$

The demonstration of this equation is as follows. Both sides of the following equation:

$$x_{s2}\left(\frac{\partial j_{2;1,3}}{\partial x_{s3}}\right)_{x_S} + x_{s3}\left(\frac{\partial j_{3;1,2}}{\partial x_{s3}}\right)_{x_S} = x_S(1-x_S)\left(\frac{\partial(j_{3;1,2}-j_{2;1,3})}{\partial x_S}\right)_{x_{s3}} \tag{143}$$

are calculated in the following way. The left-hand side is obtained by deriving partially Eq. (49) with respect to x_{s3}. The right-hand side of (143) is calculated considering that:

$$\left(\frac{\partial j_{S;1}}{\partial x_{s3}}\right)_{x_S} = \frac{\partial J}{\partial x_{s3}\partial n_S} = \frac{\partial J}{\partial n_S \partial x_{s3}} \tag{144}$$

Using (50) in (144) and cancelling common terms, Eq. (143) is obtained. Taking the limit when x_s approaches to zero when x_{s3} is kept constant in both sides of Eq. (143) and considering that:

$$\begin{aligned}&\lim_{\substack{x_S \to 0 \\ x_{s3}\ \text{constant}}} \left(\frac{\partial\left(j_{3;1,2}(x_S,x_{s3}) - j_{2;1,3}(x_S,x_{s3})\right)}{\partial x_S}\right)_{x_{s3}} \\ &= \left(\frac{\partial j_{3;1,2}(0,x_{s3})}{\partial x_S}\right)_{x_{s3}} - \left(\frac{\partial j_{2;1,3}(0,x_{s3})}{\partial x_S}\right)_{x_{s3}} = f(x_{s3})\end{aligned} \tag{145}$$

Eq. (142) is obtained.

From values of $j^o_{S;1}$ it is possible to obtain $j^{\Delta}_{2;1,3}$ and $j^{\Delta}_{3;1,2}$ by using the following equations:

$$\begin{cases} j^{\Delta}_{2;1,3} = j^o_{S;1} - x_{s3}\dfrac{dj^o_{S;1}}{dx_{s3}} \\ j^{\Delta}_{3;1,2} = j^o_{S;1} + (1-x_{s3})\dfrac{dj^o_{S;1}}{dx_{s3}} \end{cases} \tag{146}$$

Eq. (146) was obtained by differentiating Eq. (135) with respect to x_{s3}, considering Eq. (142) and combining the result with Eq. (135).

5.2.3. Application of the limits of type II to the study of polymeric particles

The polymeric particles used were synthesized with a gradient of concentration of functional groups (acrylic acid) inside the particle [9]. In this system, the content of acrylic acid represents the polar groups, while poly(butyl acrylate-co-methylmethacrylate) is the non-polar groups. As seen in **Figure 1C** and **D**, component 1 is water, component 2 is non-polar groups and component 3 is polar groups. The polymeric particle (composed of polar and non-polar groups) is taken as a fraction "P" of the system where the variable $t_{p3} = n_3/(n_2+n_3)$ will be the mass fraction of polar groups in the particle. In this study [9], the same experimental equipment than in Section 4.4.1 was used and measurements of density and sound speed were carried out by titrating water (in the cell) with latex of polymeric particles (in the syringe). **Figure 7A** and **B** shows the density ρ and u as functions of the concentration for several values of t_{p3}. The density and sound speed were transformed into specific volumes and specific adiabatic compressibilities by using Eqs. (95) and (96), and results are shown in **Figure 1C** and **D**.

In this case, Eq. (133) will take the form:

$$j = j_1 + (j^o_{P;1} - j_1)\, t_P \tag{147}$$

and considering that $t_1 = 1 - t_P$, Eq. (147) transforms into:

$$j = j^o_{P;1} + (j_1 - j^o_{P;1})\, t_1 \tag{148}$$

Using Eq. (148) as a fit function in **Figure 8C** and **D**, the partial specific volume at infinite dilution of the particles ($v^o_{P;1}$) and the partial specific adiabatic compressibility at infinite dilution of the particles ($k^o_{S\,P;1}$) were obtained from the independent term of Eq. (148) and the results are shown in **Figure 9A** and **B** as functions of t_{p3}. In this case, Eqs. (100) and (101) take the form:

$$v^o_{P;1} = v^o_{P;1/atom} + v^o_{P;1/free} + v^o_{P;1/hyd} \tag{149}$$

$$k^o_{S\,P;1} = k^o_{S\,P;1/free} + k^o_{S\,P;1/hyd} \tag{150}$$

The partial specific properties of polar ($j^{\Delta}_{3;1,2}$) and non-polar ($j^{\Delta}_{2;1,3}$) groups were calculated by using Eq. (146). The derivatives of Eq. (146) were calculated numerically by using schemes of finite differences. **Figure 9C** and **D** shows, as functions of the amount of polar groups (t_{p3}), the values of specific partial volumes of non-polar and polar groups, respectively. **Figure 9D** and **F** shows, respectively, the specific partial adiabatic compressibility of non-polar and polar groups.

With similar arguments than in Section 4.4.1, we can get the following equations for the volumes:

$$v^{\Delta}_{2;1,3} = v^{\Delta}_{2;1,3/atom} + v^{\Delta}_{2;1,3/free} + v^{\Delta}_{2;1,3/hyd} \tag{151}$$

$$v^{\Delta}_{3;1,2} = v^{\Delta}_{3;1,2/atom} + v^{\Delta}_{3;1,2/free} + v^{\Delta}_{3;1,2/hyd} \tag{152}$$

and for the adiabatic compressibilities:

$$k^{\Delta}_{T\;2;1,3} = k^{\Delta}_{T\;2;1,3/free} + k^{\Delta}_{T\;2;1,3/hyd} \tag{153}$$

$$k^{\Delta}_{T\;3;1,2} = k^{\Delta}_{T\;3;1,2/free} + k^{\Delta}_{T\;3;1,2/hyd} \tag{154}$$

In addition to this, by combining Eqs. (135), (149), (151) and (152), one gets the following equations:

$$v^o_{P;1/atom} = t_{p2} v^{\Delta}_{2;1,3/atom} + t_{p3} v^{\Delta}_{3;1,2/atom} \tag{155}$$

$$v^o_{P;1/free} = t_{p2} v^{\Delta}_{2;1,3/free} + t_{p3} v^{\Delta}_{3;1,2/free} \tag{156}$$

$$v^o_{P;1/hyd} = t_{p2} v^{\Delta}_{2;1,3/hyd} + t_{p3} v^{\Delta}_{3;1,2/hyd} \tag{157}$$

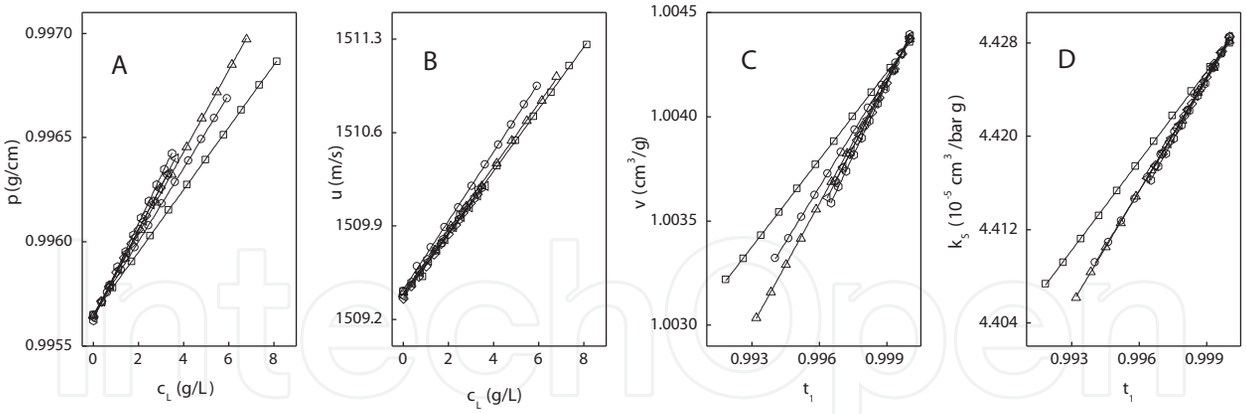

Figure 8. (A) Density of latex as function of polymeric particles concentration. (B) Sound speed as function of polymeric particles concentration. (C) Specific volume of latex as function of mass fraction of solvent (water). (D) Specific adiabatic compressibility as function of the mass fraction of solvent (water). In all figures (□) 0 wt%, (○) 5wt%, (Δ) 10 wt%, (◊) 15 wt %, (◁) 20 wt%, (⬢) 25wt%.

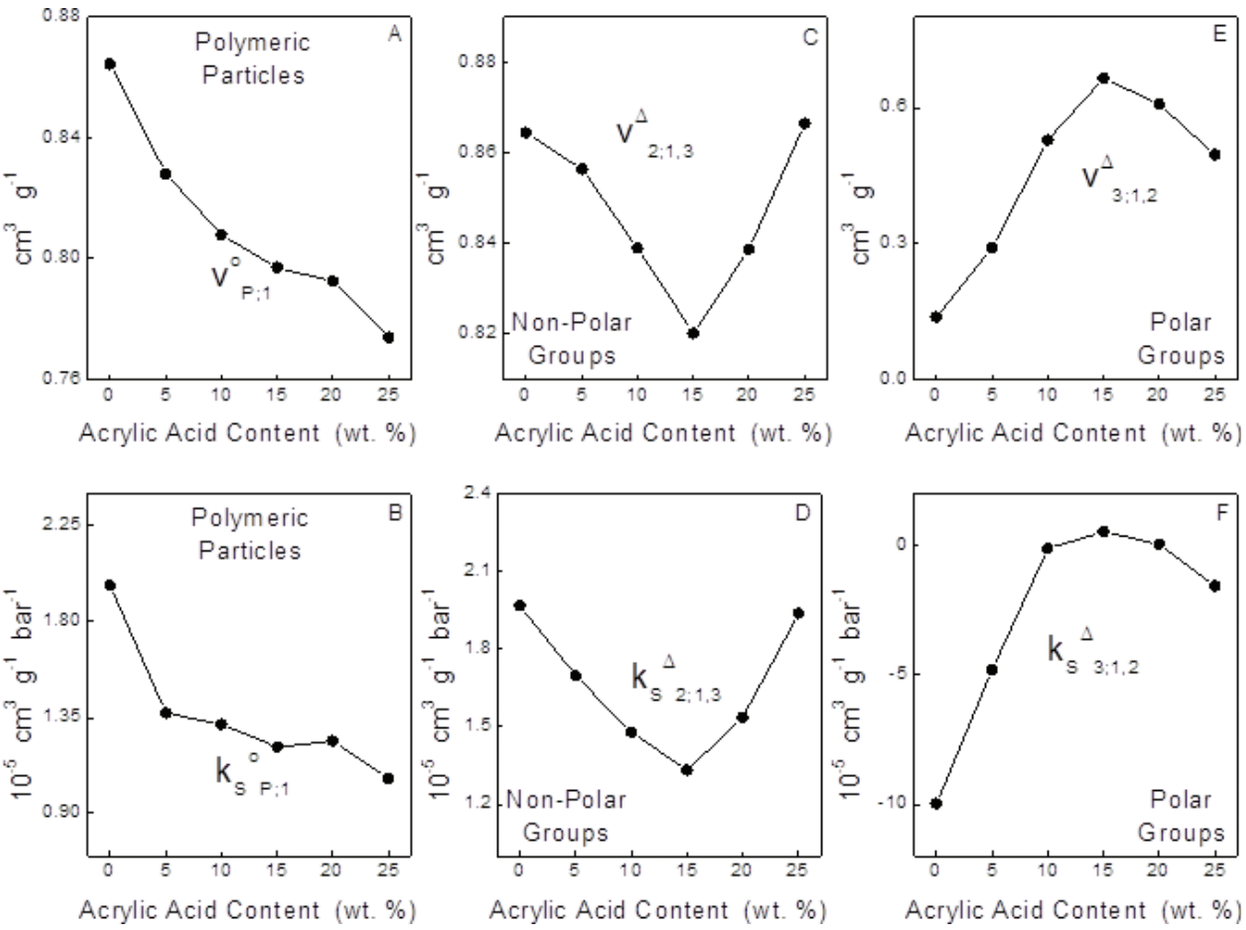

Figure 9. (A) Partial specific volume of the polymeric particles at infinite dilution as function of the polar group content. (B) Partial specific adiabatic compressibility of particles at infinite dilution as function of the polar group content. (C) Partial specific volume of non-polar groups at infinite dilution as function of the polar group content. (D) Partial specific adiabatic compressibility of non-polar groups at infinite dilution as function of the polar group content. (E) Partial specific volume of polar groups at infinite dilution as function of the polar group content. (F) Partial specific adiabatic compressibility of polar groups at infinite dilution as function of the polar group content.

where similar equations can be obtained for the adiabatic compressibilities. **Figure 9A** and **B** shows that $v^{o}_{P;1}$ and $k^{o}_{sP;1}$ decrease when the amount of polar groups increases. This fact indicates an increment of the hydration in the interior of the particle when the amount of polar groups increases. The distribution of this hydration is as follows. **Figure 9C** and **D** shows that $v^{\Delta}_{2;1,3}$ and $k^{\Delta}_{s2;1,3}$ decrease from 0 to 15% of polar groups, while **Figure 9E** and **F** shows that $v^{\Delta}_{3;1,2}$ and $k^{\Delta}_{s3;1,2}$ increase. This fact can be interpreted because the hydration is redistributed from the polar groups to the non-polar groups. In the region of 15–25%, this behaviour is reversed.

6. Conclusions

In this chapter, we have developed common thermodynamic bases for isothermal titration calorimetry, densimetry and measurement of sound speed in terms of thermodynamic partial properties (interaction partial enthalpies, partial volumes and partial adiabatic compressibilities). To build these common thermodynamic bases, it is necessary to introduce new concepts, i.e., the concept of fraction of a system and the concept of thermodynamic interaction between components of a system. An advantage of the proposed thermodynamic scheme is the possibility of including new thermodynamic partial properties as partial heat capacities.

Author details

Mónica Corea[1], Jean-Pierre E. Grolier[2] and José Manuel del Río[3]*

*Address all correspondence to: jm.delrio.garcia@gmail.com

1 National Polytechnic Institute, Mexico City, Mexico

2 Institut de Chimie de Clermont-Ferrand UMR 6296, Aubière Cedex, France

3 Petroleum Mexican Institute, Mexico City, Mexico

References

[1] do Carmo MP, editor. Differential Geometry of Curves and Surfaces. 2nd ed. Englewood Cliffs, New Jersey: Prentice-Hall, Inc.; 1976. p. 503

[2] Callen HB, editor. Thermodynamics and an Introduction to Thermostatics. 2nd ed. New York: John Wiley & Sons; 1985. p. 493

[3] Klotz IM, Rosenberg RM, editors. Chemical Thermodynamics: Basic Theory and Methods. 6th ed. New York: Wiley-Interscience; 2000. p. 556

[4] del Río JM, Santillan R, Vallejo I, Grolier J-PE, Jiménez-Ángeles F, Corea M. A thermodynamic method to study the interaction between NaOH and highly carboxylated polymeric particles in solution. Journal of Solution Chemistry. 2015;**44**:963–986

[5] Grolier J-PE, del Río JM. On the physical meaning of the isothermal titration calorimetry measurements in calorimeters with full cells. International Journal of Molecular Sciences. 2009;**10**:5296–5325

[6] Perez A, Ruíz A, Santillán R, del Río JM, Corea M. Partial volume and compressibility at infinite dilution. Reactive & Functional Polymers. 2008;**68**:1422–1428

[7] Santillán S, Nieves E, Alejandre R, Pérez E, del Río JM, Corea M. Comparative thermodynamic study of functional polymeric latex particles with different morphologies. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2014;**444**:189–208

[8] Chalikian TV, Sarvazyan AP, Breslauer KJ. Partial molar volumes, expansibilities, and compressibilities of alpha, omega amino carboxylic acids in aqueous solutions between 18 and 55°. Journal of Physical Chemistry. 1997;**97**:13017–13026

[9] Gekko K, Noguchi H. Compressibility of globular proteins in water at 25°C. Journal of Physical Chemistry. 1979;**83**:2706–2714

[10] Gekko K, Hasegawa Y. Compressibility—Structure relationship of globular proteins. Biochemistry. 1986;**25**:6563–6571

[11] Kauzmann W. Some factors in the interpretation of protein denaturation. Advances in Protein Chemistry. 1959;**14**:1–63

[12] Reisler E, Haik Y, Eisenberg H. Bovine serum albumin in aqueous guanidine hydrochloride solutions. Preferential and absolute interactions and comparison with other systems. Biochemistry. 1977;**16**:197–203

[13] Chalikian TV, Sarvazyan AP, Breslauer K. Hydration and partial compressibility of biological compounds. Journal of Biophysical Chemistry. 1994;**51**:89–109

[14] Clarke RG, Tremaine PR. Amino acids under hydrothermal conditions: Apparent molar volumes of aqueous alpha-alanine, beta-alanine, and proline at temperatures from 298 to 523 K and pressures up to 20.0 MPa. Journal of Physical Chemistry B. 1999;**103**:5131–5144

[15] Lo Surdo A, Shin C, Millero FJ. The apparent molal volume and adiabatic compressibility of some organic solutes in water at 25°C. Journal of Chemical & Engineering Data. 1978;**23**:197–201

[16] Gekko K, Yamagami K. Flexibility of food proteins as revealed by compressibility. Journal of Agricultural and Food Chemistry. 1991;**39**:57–62

[17] Chalikian TV, Totrov M, Abagyan R, Breslauer KJ. The hydration of globular-proteins as derived from volume and compressibility measurements—Cross correlating thermodynamic and structural data. Journal of Molecular Biology. 1996;**260**:588–603

[18] Gekko K, Kimoto A, Kamiyama T. Effects of disulfide bonds on compactness of protein molecules revealed by volume, compressibility, and expansibility changes during reduction. Biochemistry. 2003;**42**:13746–13753

[19] Dubins DN, Filfil R, Macgregor RB Jr, Chalikian TV. Role of water in protein-ligand interactions: Volumetric characterization of the binding of 2′-CMP and 3′CMP to ribonuclease A. Journal of Physical Chemistry B. 2000;**104**:390–401

[20] Grolier J-PE, del Rio JM. Isothermal titration calorimetry: A thermodynamic interpretation of measurements. Journal of Chemical Thermodynamics. 2012;**55**:193–202

[21] Grolier J-PE, del Rio JM. Isothermal titration calorimetry: Application of the Gibbs-Duhem equation to the study of the relationship between forward and reverse titrations. Journal of Solution Chemistry. 2014;**44**:987–1003

IntechOpen