

Equilibrium model for agglomeration phenomena in solid polydispersions subject to adsorption from liquid solution

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A general thermodynamic-electrochemical model, supported by an experimental titration procedure, is proposed to determine the number of solid aggregates of a polydispersed (and/or colloidal) system in a liquid medium subject to simultaneous agglomeration phenomena and adsorption of H^+ and/or OH^- ions from solution and endowed with an interparticle potential which is not strongly attractive. In a previous work [D. Beruto, S. Mezzasalma, and D. Baldovino, *J. Chem. Soc. Faraday Trans. 2* **91**, 323 (1995)] adsorptions of protons and/or oxidyles onto the solid surfaces of monomodal silicon nitride aqueous dispersions were obtained by titration measurements made with a metal-oxide-semiconductor ion-sensitive field-effect transistor *pH*-meter device and employed to obtain the number of solid aggregates from the thermodynamic equilibrium state of the slurries, derived from the total Gibbs function. More generally, to apply the same titration procedure to liquid dispersions involving many solid phases, it is shown here that a simple partition criterion can be defined to obtain the experimental adsorption data related to each solid phase of the polydispersed system. Theoretically, the equilibrium state is achieved from the total Gibbs free function of the slurries with respect to each single solid aggregate species and to the "mixed" aggregates, containing all solid phases. To this end, following the Derjaguin-Landau-Verwey-Overbeek theory, Coulombic charge-charge interactions and dispersion-force effects, other than general multipole contributions among mixed clusters, are considered as not too strong perturbations of the ideal Gibbs free energy. By inserting the titration data in the physico-chemical condition theoretically derived, it is possible to obtain all numbers of solid aggregates as a function of the electrolyte concentration (*pH*) in the liquid solution. [S1063-651X(97)07304-2]

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INTRODUCTION

Solid polydispersion (and monodispersion) in a liquid medium is a topic of great interest in the branch of condensed matter and granular solids physics [2–11] as well as in several important applications in materials science [12–20]. However, the notable complexity of the solid agglomeration mechanisms, jointly with the complex system of interactions among solid aggregates and/or molecules immersed in a liquid medium [21–27], makes it very difficult to know the exact physico-chemical properties of such systems. Both thermodynamic [10,28], and kinetics [10,29], theories have been developed to explain equilibrium and nonequilibrium solid agglomeration phenomena and, recently [30], the interfacial solid-liquid surface tension has been proposed as a very important driving force in solid aggregation phenomena. Nevertheless, although the new geometrical approaches [fractal growth models, i.e., diffusion-limited aggregation (DLA), cluster-cluster aggregation (CA), and lattice animals (LA) models, percolation theory, etc.] and the increased knowledge of the interactions occurring in a suspension have brought considerable progress, there are many open questions [10,21]. Particularly, it is a very tough task to relate the experimental measurements to the theoretical model of a solid poly-monodispersion. Often, only sophisticated experimental techniques [31] [electron spectroscopy for chemical analysis] (ESCA), neutron and light scattering, fluorocarbon surfactant solutions, laser cleaning, various electrokinetics and electrophoretic methods, etc. are helpful to verify complex theories, involving quantities which are not easily ac-

cessible. On such a basis, this work is intended to contribute to the theoretical study of a solid polyphasic suspension employing quantities relatively easy to detect experimentally. To this aim, for the sake of simplicity, only dispersed systems reaching equilibrium will be studied in the following. A method to investigate the average number and dimensions of solid aggregates belonging to one solid phase dispersed in a liquid medium was recently proposed [1]. A titration procedure, improved by a metal-oxide-semiconductor ion-sensitive field-effect transistor (MOS-ISFET) *pH*-meter device, made it possible to quantify and characterize the adsorption process of H^+ and OH^- ions onto a solid Si_3N_4 surface. Subsequently, by using these data to evaluate the total Gibbs free energy of the suspension, the number of solid aggregates was derived, from the equilibrium state at constant pressure and constant temperature, for different liquid phase *pH* values and different solid mass concentrations. In this paper the method is extended in general to (colloidal) mixtures of several solid phases dispersed in liquids. From a thermodynamic point of view, when solid monophasic suspensions were investigated, only the predominant Coulombic charge-charge repulsion had to be considered to write the Gibbs free energy correctly [1,32,33]; in fact, the orders of magnitude of the average numbers ($\approx 10^4$ – 10^8 cm^{-3}), average size (≈ 1 – $20\mu m$) and average surface charge density ($\leq \pm 400\mu C/cm^2$) of solid agglomerates were consistent with the current literature as well as with direct light scattering measurement [34]. In solid polydispersed systems, to describe the formation of the mixed clusters containing all kinds of solid phases, the dispersion forces [21,32,35–37]

[see Derjaguin-Landau-Verwey-Overbeek (DLVO) theory] must necessarily be considered; moreover, as a consequence of asymmetric surface charge distributions, which may occur by different adsorption and agglomeration mechanisms, electrostatic multipole contributions must be expected [38,39]. Experimentally, the simultaneous description of adsorption phenomena is required to solve the equilibrium condition derived with respect to each kind of solid aggregate species. The model developed here was recently applied to solid bimodal $\text{Si}_3\text{N}_4 + \text{Al}_2\text{O}_3/\text{H}_2\text{O}$ (l) dispersions [40], and the derived orders of magnitude of the average numbers, average size, and surface charge density again agree with those arrived at by direct measurement. Moreover, the necessity of taking into account aggregation models based on a stochastic random-walk agglomeration mechanism [9,10,41] emerged from such an application.

THE EXPERIMENTAL METHOD

Solid monophasic dispersion. The titration procedure employed to deal with the evolution of the surface charges of solid monophasic liquid dispersions with the variation in the liquid phase $p\text{H}$ has been widely explained elsewhere [1,30,40,42–44] for $\text{Si}_3\text{N}_4/\text{H}_2\text{O}$ (l) suspensions. For the present more general case, it is sufficient to recall the following. By addition of small amounts of electrolyte solution, the liquid phase $p\text{H}$ was changed progressively by one-unit steps. Measurements were carried out with a MOS-ISFET $p\text{H}$ -meter device [1,45], unable to detect the H^+ and/or OH^- ions adsorbed from the aqueous solution onto the agglomerate solid surface by usual surface ionization-complexation phenomena [17–21]. Accordingly, it is possible to characterize the small ion H^+ and/or OH^- adsorption at the solid-liquid interface. In fact, if the ionic activities do not change sensibly during the titration procedure, the ions left in the liquid medium n_l and those adsorbed onto the solid aggregate n_a can be separated by the mass balance of all ions added to the slurry and, from the charge balance, by

$$n_l = 2n_s + n_a, \quad (1)$$

where $n_s = \aleph(V+v)c$ is related to the change in the suspension $p\text{H}$ value; it involves Avogadro's number \aleph , the electrolyte concentration $c (= 10^{-p\text{H}_3\text{O}^+ / -p\text{OH}^-})$, the suspension volume V , and the electrolyte volume added to the slurry v . The meaning of n_a and n_l must be determined. In another work [30] it has been shown that the n_a vs $p\text{H}$ curve is equivalent to the H^+ and/or OH^- ion adsorption isotherm and therefore it reflects the physico-chemical mechanism of the surface covering. On the other hand, the total number n_l is related to the Debye-Hückel constant of the dispersion which characterizes the depth of the Stern double layer [43]. Typical behaviors of n_a vs the suspension $p\text{H}$ are shown in Fig. 1, where the number of adsorbed ions is a function monotonically increasing in the electrolyte concentration in both acid and basic environments; the $p\text{H}$ value corresponding to the minimum in n_a is here [1] the point of null surface

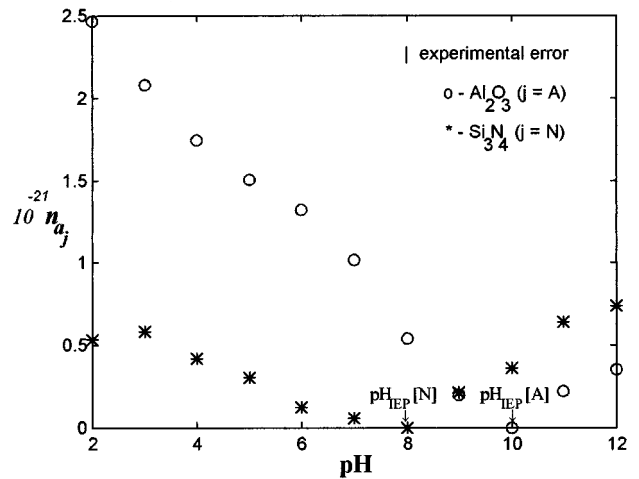
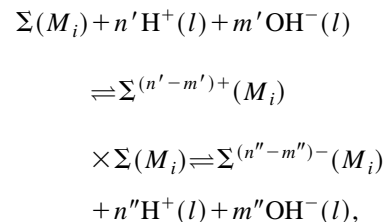


FIG. 1. Cumulative number of ions $n_{a_N}(10^{-21})$ and $n_{a_A}(10^{-21})$ adsorbed from aqueous solution onto (a) silicon nitride $[\text{N}]$ ($-* -$) and (b) alumina $[\text{A}]$ ($-\circ -$) solid surface of monophasic suspensions at solid mass concentration $c_{N,A} = 0.5$ and dispersed in $V = 35 \text{ cm}^3$. Titration measurements were conducted by using amounts of $1\text{N HNO}_3/\text{NaOH}$ solutions in the acid-basic environment.

charge, usually called the isoelectric point ($p\text{H}_{\text{IEP}}$). The behaviors of n_l vs $p\text{H}$ and n_s vs $p\text{H}$ are quite similar to the previous n_a vs $p\text{H}$ in Fig. 1.

Solid polyphasic dispersion. More generally, it is possible to extend the method to solid polyphasic dispersions in liquids according to the following steps. Let $M_i[m_i; w_N, c_k]$ be a solid monodispersed system, formed by a solid substance M_i of mass m_i at a solid mass concentration μ_N and by a liquid medium at an electrolyte concentration $c = c_k$, and let $n_{a_i}(M_i)$ be the number of H^+ and/or OH^- ions adsorbed from the solution onto the i th solid surface sites during the k th step of the titration procedure according to a general local surface chemistry given schematically by [1,42,46]



where l denotes the bulk phase and $\Sigma(M_i)$ is the set of all neutral and charged sites, depending on the solid surface features of M_i (see Fig. 2). In the solid polydispersed suspension M given by the sum of all monophasic systems:

$$\begin{aligned} M[m; \mu_N, c_k^{(m)}] &= \sum_i M_i[m_i; \mu_N, c_k], \\ m &= \sum_i m_i, c_k^{(m)} = c_k \end{aligned} \quad (2)$$

if $\tilde{n}_a^{(m)}$ denotes the total number of adsorbed H^+ and/or OH^- ions at the k th titration step, the number of ions

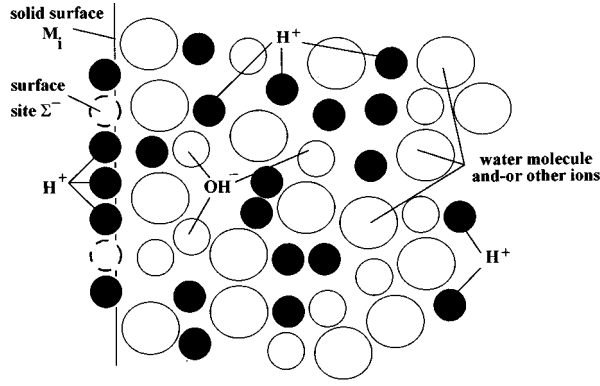


FIG. 2. Scheme of the surface ionization phenomena in aqueous media.

$n_a(j, M)$ adsorbed onto the M_j solid surface species in the multimodal system M can be assumed to be equal to

$$n_a(j, M) = \rho_j \tilde{n}_a(M), \quad (3)$$

where ρ_j denotes the j th partition coefficient, which is the probability that an adsorption or desorption event in the polydispersion M occurs at the j th solid surface. For a perfectly inert system, where solubility products [47] are absent, the adsorption or desorption event must obey the conservation law represented by the completeness of the partition probability set, namely, $\sum_j \rho_j \equiv 1$. When a noninert suspension is concerned, the new coefficients ρ'_j must be completed by a ‘‘loss’’ term, generally dependent on the electrolyte concentration $\sigma = \sigma(c)$, and such that $\sigma + \sum_j \rho'_j \equiv 1$. Accordingly, setting $\sigma = 0$, from the ionic mass balance [1] applied to Eq. (2), these values are obtained as

$$\rho_j = \frac{n_{a_j}(M_j)}{\sum_i n_{a_i}(M_i)}. \quad (4)$$

Since charge and mass balance equations of the form (1) are valid both for $n_{a_j}(M_j)$ and $\tilde{n}_a(M)$, it is important to emphasize that the experimental procedure performed for a solid monophasic suspension does not change when polyphasic systems are titrated. Assumption of the partition coefficient set $\{\rho_j\}$ permits use of the global titration data which derive from the MOS or ISFET-based pH measurements in a solid polyphasic system. Titration measurements involving partition coefficients defined in Eqs. (3) and (4) were recently improved for solid biphasic ceramic suspensions [40]

THEORY—DERIVATION OF THE EQUILIBRIUM STATE

Solid monophasic dispersed system. Consider a solid monodispersed system immersed in a liquid medium. To write the total Gibbs free energy G_1 it is sufficient to consider the mixing entropy and the formation energy of all particle species—ions, solvent molecules, and solid aggregates—and the Coulombic term δG_{el} , which represents the weak correction to the unperturbed system: [1,32,33]

$$\tilde{G}_1 = G_1 + \delta G_1^{(el)}, \quad (5)$$

where

$$G_1 = N_s g_s + \sum_j \tilde{g}_j, \quad \tilde{g}_j = \left(K T \ln \frac{n_j}{e N_s} + g_j \right) n_j \quad (6)$$

and K is the Boltzmann constant, T the absolute temperature, N_s the number of solute molecules having a specific energy g_s , n_j the number of particles of the j th species, and g_j the related specific formation energy [33,48]. The electrostatic perturbation follows the Debye-Hückel theory [17–21,33]:

$$\delta G_1^{(el)} = -Q_{el} \left(\sum_j n_j z_j^2 \right)^{3/2}, \quad (7)$$

where z_j is the j th ionic valency number and $Q_{el} = 2/3 [(\pi/VKT)(q_e/\epsilon)^3]^{1/2}$ is a factor dependent on the electronic charge q_e , on the slurry volume, and on the absolute dielectric function ϵ of the medium. In a previous paper, to obtain the equilibrium state for one solid aggregate kind, it was sufficient to take into consideration the equilibrium condition which results from the Gibbs function with respect to the ions adsorbed at the solid-liquid interface or, equivalently [1], with respect to the ions left in the solution. For a population of N_s solvent molecules, n_j ions in the liquid medium, and \bar{n}_p solid aggregates, this condition is [1,30,42]

$$\left(\frac{\partial \tilde{G}_1}{\partial n_l} \right)_{T, P, \{n_k\}_{k \neq l}} = 0, \quad (8)$$

which yields

$$K T \ln \frac{n_l}{N_s} + \bar{g}_l = Q_{el} (2 \bar{z}_p - 1) (n_a \bar{z}_p + n_l)^{1/2}, \quad (9)$$

where \bar{z}_p is the average valency number of the solid aggregate:

$$\bar{z}_p \approx \pm \frac{n_a}{\bar{n}_p}. \quad (10)$$

Equation (9) was solved to obtain the average number of solid aggregates \bar{n}_p , once n_a and n_l were known from the titration data. Typical behaviors of the number of solid aggregates versus the suspension pH , here derived from the experimental data relative to those shown in Fig. 1, are reported in Fig. 3. It can be noted that, with the increasing of the net surface charge or, equivalently, of the repulsive interaction among aggregates, the dispersion degree increases. Accordingly, since $V = \text{const}$, the average size decreases with the pH and it is maximum at the isoelectric point of the slurry.

Solid polyphasic dispersed system. In the present case, when m solid phases are concerned, to describe the global agglomeration processes (involving identical and different solid species), the London-van der Waals interactions $\delta G_m^{(H)}$ must be taken into account in the total free Gibbs energy \tilde{G}_m of the system [17–21,35–37].

$$\tilde{G}_m = G_m + \delta G_m^{(el)} + \delta G_m^{(H)}, \quad (11)$$

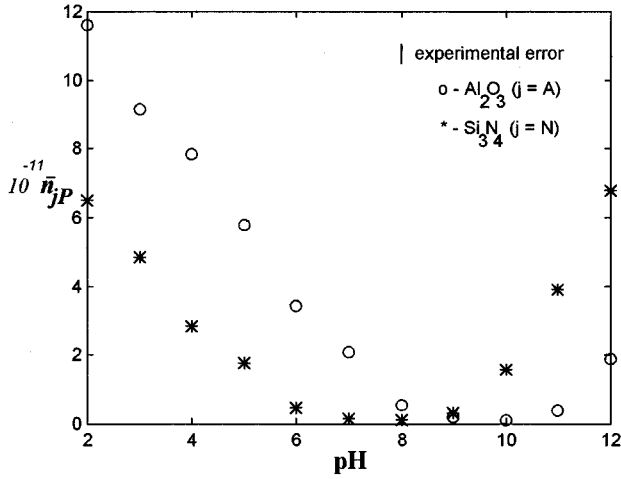


FIG. 3. Cumulative number of solid aggregates $\bar{n}_{NP}(10^{-11})$ and $\bar{n}_{AP}(10^{-11})$ in silicon nitride and alumina monophasic aqueous suspensions at total solid mass concentration equal to 0.5, dispersed in $V=35 \text{ cm}^3$ and titrated by using 1N HNO_3/NaOH solutions (see Fig. 1).

where, under the constraint $|\delta G^{(\text{el})} + \delta G_m^{(H)}| \gg KT$ that is equivalent to binding energies not too high with respect to the temperature (KT), reversible aggregation is expected [10,28]. Equation (11), which replaces Eq. (5), is a function of the m -modal set $\{\bar{n}_{jP}\}_{j=1}^m$ of monophasic solid aggregates; thus, to achieve the equilibrium state, conditions other than Eq. (8),

$$\left(\frac{\partial \tilde{G}_m}{\partial n_l} \right)_{T,P,\{n_k\}_{k \neq l}} = 0, \quad (12)$$

must be found. To this end, consider a distribution of mixed clusters formed by all m solid aggregate species that are held together by the long-range dispersion forces [17–21,35–37]. Accordingly, when adsorption and agglomeration-deagglomeration phenomena are near the equilibrium state, the number of mixed clusters approaches an average value \bar{n}_{vP} given by

$$\bar{n}_{vP} = \frac{\bar{n}_{jP}}{\bar{v}_j} \quad \forall j = 1, \dots, m, \quad (13)$$

where \bar{v}_j is the number of j th solid aggregate species in the global mixed cluster.

At constant pressure, constant temperature, and for a constant aggregate distribution $\{\bar{n}_{kP}\}$, the previous condition holds:

$$\left(\frac{\partial \tilde{G}_m}{\partial \bar{v}_j} \right)_{T,P,\{\bar{n}_{kP}\}} = 0, \quad (14)$$

with

$$\left(\frac{\partial \bar{n}_{jP}}{\partial \bar{v}_j} \right)_{T,P,\{\bar{n}_{kP}\}} = -\frac{\bar{n}_{jP}}{\bar{v}_j^2}. \quad (15)$$

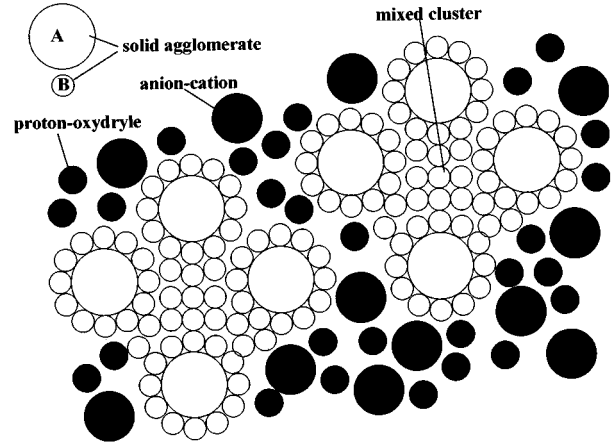


FIG. 4. Scheme of the described solid aggregation phenomena for two solid species A and B (when $\bar{v}_A=4$ and $\bar{v}_B=62$). All ions and solid aggregates are surrounded by molecules of a liquid medium (not indicated in the figure).

Therefore by the $(m+1)$ -equation system (12) and (14), the equilibrium state is described by the set $\{\bar{n}_{jP}, \bar{n}_{vP}\}$ [or equivalently, from Eq. (13), by the set $\{\bar{n}_{jP}, \bar{v}_j\}$]. It has been noted that Eqs. (12) and (14) describe the equilibrium state with respect to Eq. (1), the agglomeration process of an equivalent population of mixed clusters, and to Eq. (2), the solid surface ionization phenomena (see Fig. 4). The population of mixed solid clusters must be considered now in the development of each term of the Gibbs function \tilde{G}_m and this is a very difficult task. In the following, the effects of the solid mixed population on the mixing entropy and on the Coulombic and London–van der Waals interactions will be attempted under some reasonable assumptions. First, if only mixed clusters are considered in the entropy function, the mixing contributions of solid monophasic aggregates are lost; on the other hand, if one considers the set $\{\bar{n}_{jP}\}$ only, the partial effect of the mixed population on the total mixing driving force vanishes completely. Accordingly, the entropy should be expressed by writing the van der Waals long-range effects on the configuration integral related to the entire aggregate set $\{\bar{n}_{jP}, \bar{n}_{vP}\}$. To give the exact cluster expansion [49,50] of the entropy function is a tough task, strongly ruled by the intrinsic complexity of the agglomeration or deagglomeration mechanism. On the basis of results of several studies [21–27] and of previous papers [1,30,40–44], in which the agglomeration or adsorption antagonism was discussed, there are reasons for believing that the thermodynamic equilibrium states of a solid polydispersed system can be sensitive to the specific features of agglomeration. Thus to overcome this difficulty the equivalent mixed cluster can be regarded as the equilibrium interacting system where the influence of van der Waals interactions on the mixing entropy function must be attempted. Accordingly, as defined by the Maxwell-Boltzmann statistics [49,50], any solid aggregate species j produces a degeneracy $\bar{v}_j!$ that must be taken into account in the entropy S_m . Thus in the limit of $\bar{v}_j \gg 1$

$$S_m = KT \left(\sum_{j=1}^m \bar{n}_{jP} \ln \frac{\bar{n}_{jP}}{eN_s} - \bar{v}_j \ln \frac{\bar{v}_j}{eN_s} \right) \quad (16)$$

and, combining all formation energies and entropic terms, the old Eq. (6) can be rewritten as

$$G_m = N_s g_s + \bar{g}_l^{(m)} + \sum_{j=1}^m \bar{g}_j^{(m)}, \quad (17)$$

where

$$\begin{aligned} \bar{g}_l^{(m)} &= n_l \bar{g}_l + K T n_l \ln \frac{n_l}{e N_s}, \\ \bar{g}_j^{(m)} &= K T \left(\bar{n}_{jP} \ln \frac{\bar{n}_{jP}}{e N_s} - \frac{\bar{n}_{jP}}{\bar{n}_{vP}} \ln \frac{\bar{n}_{jP}}{e \bar{n}_{vP} N_s} \right) + \bar{n}_{jP} g_{jP}, \end{aligned} \quad (18)$$

and where g_{jP} is the formation energy of the j th solid species in the liquid medium. Secondly, the electrostatic interaction form follows from the Debye-Hückel theory [17–21,33], already adapted to solid monophasic dispersions [1] and here improved by global multipole contributions [38,39,51–53] among mixed clusters. When agglomeration phenomena of different kinds of solid atoms, molecules, and/or aggregates occur as a consequence of different adsorption and aggregation mechanisms [17,21,46,54,55], the charge distributions onto the solid surface can be considerably asymmetrical. Accordingly, as in a previous work [1], the average valency number associated with each ι th multipole contribution can be introduced as

$$\bar{\xi}_v^{(\iota)} \approx \pm \frac{\mathcal{M}_v^{(\iota)}}{\bar{n}_{vP}}, \quad (19)$$

$q_e \mathcal{M}_v^{(\iota)}$ being the amount of charge onto the solid mixed cluster related to the ι -pole interaction. Therefore recalling Eqs. (3) and (10),

$$\bar{z}_{jP} \approx \pm \frac{n_a(j)}{\bar{n}_{jP}}, \quad (20)$$

the electrostatic contribution to insert in the total Gibbs function becomes

$$\delta G_m^{(\text{el})} = -Q_{\text{el}} \left(n_l z_l^2 + \sum_{j=1}^m \frac{n_a^2(j)}{\bar{n}_{jP}} + \frac{\sum_{\iota} \mathcal{M}_v^{(\iota)2}}{\bar{n}_{vP}} \right)^{3/2}, \quad (21)$$

which can be estimated experimentally by making use of the adsorption partition probabilities $\{\rho_j\}$. Generally, in the present case, the amount of charge related to an ι -pole interaction can be expressed by functions $\mathcal{I}_\iota: \mathbb{R}^m \rightarrow \mathbb{R}$ of all partition coefficients [see Eqs. (3) and (4)]:

$$\mathcal{M}_v^{(\iota)} = \bar{n}_a \mathcal{I}_\iota(\{\rho_j\}) \quad (22)$$

so that Eq. (21) is transformed into

$$\delta G_m^{(\text{el})} = -Q_{\text{el}} \left[n_l z_l^2 + \bar{n}_a^2 \left(\sum_{j=1}^m \frac{\rho_j^2}{\bar{n}_{jP}} + \frac{\sum_{\iota} \mathcal{I}_\iota^2}{\bar{n}_{vP}} \right) \right]^{3/2} \quad (23)$$

and can be evaluated by the aforesaid electrochemical titration procedure described by Eqs. (1)–(4). The exact evaluation of multipole contributions [38,39,51–53] is a difficult task also, here strongly dependent on the adsorption mechanisms and on the agglomerate surfaces [17,21,46]. Nevertheless, without details of surface charging phenomena, as often given, it is always possible to take into account in Eq. (23) a global asymmetry charge contribution:

$$\tilde{\mathcal{I}} \sim \sum_{\{j',j''\}} \rho_{j'} - \rho_{j''} \quad (24)$$

(sum over all aggregate pairs in a mixed cluster) which estimates the differences of the adsorbed charge moduli due to the heterogeneity of the dispersion. This is the approach adopted in the recent application of the present model [40], where global dipole contributions $\tilde{\mathcal{I}}_2$ assumed the previous form (24). Thirdly, to evaluate the weak dispersion-force effect, we focus on a mixed cluster as the fundamental building block of agglomeration phenomena. Through Eqs. (13)–(18), a mixed cluster was just defined as the average portion of the total solid phase, where the agglomeration features of all m solid phases occur equivalently. Accordingly, by applying the Hamaker formula to a distribution of spherical solid aggregates, we have [17,21,32,35–37]

$$\delta G_m^{(H)} = \frac{1}{24} \sum_{\{j',j''\}} \pi_{(j',j'')} \frac{\mathcal{A}_{(j',j'')}}{\bar{x}_{(j',j'')}} \quad (25)$$

which is evaluated by summing up [56] all pairs $\pi_{(j',j'')}$ of solid aggregates per mixed cluster. In Eq. (25), $\mathcal{A}_{(j',j'')}$ is the nonretarded Hamaker constant [21,32,57,58] for the solid substances (j', j'') and $\bar{x}_{(j',j'')}$ is the average ratio between the distance from the outer surfaces and the aggregate diameter. Evaluation of Hamaker constants can be performed according to several theoretical and experimental approaches [35–37] (macroscopic and microscopic approximations, from surface tension and solid-solid interaction measurements, etc.) while [56]

$$\pi_{(j',j'')} \approx \left(1 - \frac{\delta_{j'j''}}{2} \right) \bar{v}_{j'} \bar{v}_{j''} \quad (26)$$

($\delta_{j'j''}$ is the Kronecker symbol). On the other hand, estimation of the average ratios $\bar{x}_{(rs)}$ results from the concerned (random or regular) aggregate packing characteristics. Details, here not important, are provided elsewhere [59–63]. As example, for Apollonian-based packings [62,63], namely, $\bar{x}_{(j' \neq j'')} \sim 1/2(\bar{x}_{(j'j')} + \bar{x}_{(j''j'')}) \sim (\bar{x}_{(j'j')} \bar{x}_{(j''j'')})^{1/2}$, if one applies the microscopic approximation for the Hamaker constants, namely, $\mathcal{A}_{(j',j'')} \approx \sqrt{\mathcal{A}_{(j'j')} \mathcal{A}_{(j''j'')}}$, inserting Eq. (26) in Eq. (25), the contribution of the dispersion forces reduces to the simple formula

$$\delta G_m^{(H)} \approx \frac{1}{48} \left(\sum_j v_j \sqrt{\frac{\mathcal{A}_{(jj)}}{\bar{x}_{(jj)}}} \right)^2 \quad (27)$$

Finally, according to Eq. (11), the sum of terms expressed in Eqs. (18), (23) and (27) is the total Gibbs free function of the m -phasic liquid suspension, which must be subject to the

conditions (12) and (14). Once all numbers of aggregates have been evaluated, first calculations of the average size and surface charge density result from the mass, the volume, and the charge balances [1,40,42] applied to a population of spherical aggregates. Although the assumption of spherical aggregate distributions is quite rough, it is often adopted in literature when the average size of a solid dispersion is derived from measurements of macroscopical quantities [5,7,10,11,14,16,18,31] (i.e., rheological, as viscosity and yield stress) as well as in sophisticated experimental measurements [10,31].

DISCUSSION

The theoretical and experimental method explained in the two preceding sections gives the basis for dealing with any dispersed (colloidal) system subject to relatively weak binding forces. The thermodynamic equilibrium, which was derived by improving the Debye-Hückel theory by Coulombic and dispersion potentials, might be conceived as a first step of investigation. This is not the case of the recent application [40], where preliminary yield stress measurements τ_y vs c of $\text{Si}_3\text{N}_4 + \text{Al}_2\text{O}_3/\text{H}_2\text{O}$ (l) systems showed the maximum value, the so-called τ_0 , in correspondence with $c \rightarrow 0$, thus confirming the suitability of DLVO-based interactions. Unfortunately, from a general point of view, the DLVO theory is contradicted by different studies concerning various interparticle effects. Therefore although the precise nature of several non-DLVO interactions is poor and difficult to use in performing the proposed method, a plausible second step of analysis could be represented by the addition of the numerical solution [64] of the Poisson-Boltzmann equation for the double-layer interactions to the Coulombic perturbation [see Eq. (21)] and by considering the nonretardation effects of the London-van der Waals forces [21] [see Eq. (25)]. Another matter of discussion concerns the derivation of the partition probability set $\{\rho_j\}$ as resulting from the titration procedure conducted on the single monophasic systems (ideal mixtures). This is certainly wrong when the adsorption kinetics of the solid phases mixed in the polyphasic suspension are quite different [46,65]. In such a case, to follow the single adsorption mechanism, a selective titration method is required [66]. In each case the present work is limited by the impossibility of investigating dispersed systems which are not at equilibrium. Kinetic aggregation is expected (namely, DLA and CA models) when the potential between aggregates is strongly attractive. Under less aggressive conditions, however, the repulsive Coulombic barrier is present and the growth of equilibrium structures occurs (see, for instance, the

LA model discussed in Ref. [10]). Results obtained in previous works [1,30,40,42,43] were satisfactory because the systems concerned worked in equilibrium. This has also been shown elsewhere [42] by discussing the characterization of the Si_3N_4 solid surface in water under the constraint of thermodynamic equilibrium and “true” chemical equilibrium state. Thus if reversibility is not expected the method ceases to be valid and a kinetic approach becomes necessary. When an equilibrium state strongly dependent on the kinetics is reached, it is nevertheless possible to obtain information on the kinetics history. By evaluation [67] of curves \bar{n}_{jp} vs V (V is the total suspension volume, here an independent variable) the fractal dimension of the aggregates D can be derived according to $\bar{n}_{jp} = L^D (L \sim V^{1/3})$ and, consequently, the growth of the solid-liquid surface can be estimated for different electrolyte concentration (pH) values of the liquid medium. In the end it is important to emphasize the influence of the interfacial solid-liquid surface tension as a very important driving force for the aggregation process, as recently shown elsewhere [30]. This could open a new perspective, intermediate between nonequilibrium and just equilibrium points of view.

CONCLUSIONS

- (1) A general experimental method (based on titration measurements) to quantify protons and/or oxidryle adsorption from solution onto all solid surface species in a solid polyphasic (colloidal) liquid dispersion has been formulated.
- (2) A general theory to relate adsorption (number of adsorbed H^+ and/or OH^- ions) to agglomeration phenomena (number of solid aggregates) has been achieved when not too strong attractive potentials among aggregates are concerned. It consists in deriving the thermodynamic equilibrium state that results from the total Gibbs free function of the polydispersed system.
- (3) After inserting the titration data in the equilibrium condition, the average numbers of solid monophasic aggregates and of mixed clusters containing all solid phases can be obtained as a function of the electrolyte concentration in the solution.

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