



## Phase and aggregative characterization of micellar systems

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### Abstract

It has been shown that the conditions of aggregative and phase equilibrium are realized simultaneously only at stationary points in the equilibrium size distribution curve for an aggregative system. At all other points, only the aggregative equilibrium condition holds, and a change in the chemical potentials corresponding to the phase equilibrium is entirely determined by the shape of the equilibrium distribution curve. The different forms of the equilibrium size distribution used in the theories of phase nucleation and micellization are shown to be equivalent as different forms of the mass action law. © 1997 Elsevier Science B.V.

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### 1. Introduction

Two types of polydisperse aggregative systems are the most widely known: the population of nuclei of a new phase in the process of phase transition, and associated solutions including micellar solutions. The analysis of equilibrium particle distribution in an aggregative system plays a key role in the thermodynamics and kinetics of phase transitions and micellization. The approach based on the mass action law is often opposed to the phase approach, where every particle of an aggregative system is treated as the region of a certain phase  $\alpha$  surrounded by a phase  $\beta$ , i.e. the aggregative polydisperse system is considered as being heterogeneous. In reality, the aggregative and phase equilibria are independent to a certain extent. They are not alternative approaches to the description of same facts, but different phenomena which can be combined and also can be realized separately. The delicate problem of the relation between the aggregative and phase equilibria was touched on in Refs. [1,2]; it was mainly addressed,

however, to extreme points on the equilibrium distribution curve. This paper is devoted to the analysis of the whole run of the equilibrium distribution curve from the standpoint of phase equilibrium.

### 2. The phase approach in the thermodynamics of aggregative systems

The analysis of the equilibrium distribution of particles in an aggregative system is based on the aggregative equilibrium condition

$$\mu_n = n\mu_1 \quad (1)$$

where  $\mu_n$  is the chemical potential of an aggregate consisting of  $n$  molecules,  $\mu_1$  is the chemical potential of the monomeric form of matter, and  $n$  is the aggregation number. The equilibrium distribution itself is derived from Eq. (1) [3], as well as the mass action law used especially when considering micellization in surfactant solutions [2,4]. In the

phase approach, where a polydisperse system is considered as a heterogeneous system, the ordinary phase equilibrium condition is used:

$$\mu^\alpha = \mu^\beta \quad (2)$$

Statistical mechanics gives the following expression for the chemical potential [3]:

$$\mu_n = G_n^0 + kT \ln (A_n^3 c_n f_n) \quad (3)$$

where  $G_n^0$  is the Gibbs energy for a separately taken aggregate of  $n$  molecules with resting center of mass in a pure solvent (in the absence of other aggregates),  $k$  is the Boltzmann constant,  $T$  is temperature,  $A_n \equiv \hbar(2\pi m_n kT)^{1/2}$  is the mean de Broglie wavelength for a given aggregate ( $\hbar$  is Planck's constant,  $m_n$  is the aggregate mass), and  $c_n$  and  $f_n$  are its concentration and activity coefficient, respectively. The quantity  $A_n^{-3}$  is the partition function for the aggregate translational motion. Correspondingly,  $kT \ln A_n^3$  is the contribution to the free energy from the translational motion. Similarly,  $kT \ln f_n$  represents the contribution from the interaction between aggregates, including monomers. Uniting  $kT \ln (A_n^3 f_n)$  and  $G_n^0$ , we write Eq. (3) as:

$$\mu_n = G_n + kT \ln c_n \quad (4)$$

where  $G_n$  is the Gibbs energy related to a moving and interacting aggregate.

Following the usual formalism of the thermodynamics of a small spherical particle [5], we may write:

$$G_n = \sigma A/3 + \mu^\alpha n \quad (5)$$

where  $\sigma$  is the surface tension of an aggregate,  $A$  is its surface area (to be more exact, the area of the surface of tension), and  $\mu^\alpha$  is the chemical potential of molecules in the internal phase  $\alpha$  of the aggregate. We emphasize that all the quantities in Eq. (5) refer to a real, moving and interacting aggregate (a similar expression may be written for an aggregate with resting centre of mass [5]: it is of the same form, but with different values of the quantities). The Gibbs–Duhem equation will also be needed for a spherical and equilibrium (inside it) disperse particle [6]:

$$d(\sigma A/3) + n d\mu^\alpha = 0 \quad (6)$$

Differentiating Eq. (4) with respect to  $n$  with Eqs. (5) and (6) in mind, we obtain:

$$d\mu_n/dn = \mu^\alpha + kT d \ln c_n/dn \quad (7)$$

In contrast, differentiating Eq. (1) along the distribution curve (i.e. at constant  $\mu_1$ ), we find:

$$d\mu_n/dn = \mu_1 = \mu^\beta \quad (8)$$

where the self-evident condition  $\mu_1 = \mu^\beta$  has been used since the monomers are situated automatically in the outer phase  $\beta$ . Comparing Eq. (7) and Eq. (8), we arrive at a remarkable relationship:

$$\mu^\alpha + kT d \ln c_n/dn = \mu^\beta \quad (9)$$

which shows that the condition of phase equilibrium (Eq. (2)) is realized only at the points in the equilibrium distribution curve where the condition  $d \ln c_n/dn = 0$  is satisfied. These may be extreme points for concentration or inflection points in the  $c_n(n)$  curve with a horizontal tangent. A maximum of  $c_n$ , for example, corresponds to micelles. A minimum of  $c_n$  corresponds to equilibrium Gibbs–Volmer nuclei in the population of nuclei of a new phase. An inflection point corresponds to the boundary state (for example, to the critical micelle concentration [7]).

Since  $\mu^\beta = \mu_1$ , this quantity remains constant on moving along the distribution curve at a given physical state of a system. Then, differentiating Eq. (9) along the distribution curve, we obtain the condition:

$$d\mu^\alpha/dn = -kT d^2 \ln c_n/dn^2 \quad (10)$$

from which it is seen that the shape of the distribution curve determines completely the change in chemical potential  $\mu^\alpha$  at each point of the curve. If the curve is plotted as  $\ln c_n$  versus  $n$ , then  $\mu^\alpha$  increases at convex parts and decreases at concave parts of the curve with increasing the aggregation number  $n$ . Inflection points correspond to extremes of chemical potential. If the curve is plotted as  $c_n$  versus  $n$ , then  $\mu^\alpha$  increases by necessity with  $n$  at convex parts of the curve: the transition from increasing to decreasing can occur only at a concave part.

Thus, we arrive at the following conclusion. The conditions of aggregative equilibrium and phase equilibrium are realized simultaneously only at

stationary points in the equilibrium size distribution curve for particles in a polydisperse aggregative system. Only the aggregative equilibrium condition holds at all other points, and the change in the chemical potential corresponding to phase equilibrium is completely determined by the shape of the distribution curve.

### 3. Two kinds of size distribution in aggregative systems

Although both nucleation and micellization are aggregative processes, the theories for this two related phenomena were developed differently. The widely known Volmer–Bekker–Döring–Frenkel–Zeldovich theory of phase nucleation operates with the size distribution:

$$c_n = c_1 \exp(-W) \quad (11)$$

where  $W$  is the work of formation of a molecular aggregate with the aggregation number  $n$  written in  $kT$  units. However, the theory of micellization (and association in solutions at all) rests on the mass action law leading to the distribution:

$$c_n = c_1^n \exp(-W_s) \quad (12)$$

where  $W_s$  is the standard work of aggregation. Eqs. (11) and (12) look quite incompatible, which would make Eq. (11) questionable, but this is not the case. We shall now consider the interrelation between Eqs. (11) and (12), and demonstrate that Eq. (11) is also a form of the mass action law with a differently chosen standard work.

The process of formation of molecular aggregates in solution typically proceeds at constant temperature and pressure, so the minimum work of the process is given by a change in the Gibbs energy:

$$dG = \sum_{n>1} \mu_n dN_n + \mu_1 dN_1 \quad (13)$$

where  $N_n$  is the number of aggregates with the aggregation number  $n$ . Using the mass balance equation

$$\sum_{n>1} n dN_n + dN_1 = 0 \quad (14)$$

we obtain from Eq. (13) the relationship [4]:

$$\partial G / \partial N_n = \mu_n - n\mu_1 \equiv -A_n \quad (15)$$

where  $A_n$  is the affinity of aggregation. As in chemical kinetics, the sign of affinity coincides with the sign of rate of the process: the aggregation proceeds if  $A_n > 0$  and  $\partial G / \partial N_n < 0$ , and the disaggregation proceeds if  $A_n < 0$  and  $\partial G / \partial N_n > 0$ .

Eq. (15) implies a system to be in equilibrium in all respects except the aggregative equilibrium. For a completely equilibrium aggregative system, the affinity is zero (which corresponds to a minimum of the Gibbs energy), and Eq. (15) leads to Eq. (1) containing the mass action law. To write the latter, the chemical potentials are typically represented in the form:

$$\mu_n = \mu_{ns} + kT \ln(c_n/c_s) \quad (16)$$

$$\mu_1 = \mu_{1s} + kT \ln(c_1/c_s) \quad (17)$$

where  $c_n$  and  $c_1$  are the concentrations of molecular aggregates and monomeric molecules, respectively, and  $\mu_{ns}$  and  $\mu_{1s}$  are the chemical potential values corresponding to a standard concentration  $c_s$ , but with real activity coefficients.

The mass action law follows from Eq. (1), (16) and (17):

$$c_n/c_s = K(c_1/c_s)^n, \quad K \equiv \exp[(n\mu_{1s} - \mu_{ns})/kT] \quad (18)$$

Since the coefficient  $K$  includes the activity coefficients,  $K$  is, strictly speaking, not a constant, but very close to be a constant as a detailed analysis shows [4]. As is seen from Eq. (18),  $\ln K$  yields the standard affinity of aggregation and  $-\ln K$  yields the standard work of aggregation, both being expressed in the thermal units  $kT$ .

To concretise the mass action law, one has to choose a standard concentration. This procedure influences the value of the coefficient  $K$ . The most typical choice for surfactant solutions is to set  $c_s = 1 \text{ mol l}^{-1}$ , which transforms the mass action law to:

$$c_n = K_M c_1^n \quad (19)$$

with a particular coefficient  $K_M$  and the dimensionless quantities  $c_n$  and  $c_1$  numerically equal to molarities. Another choice, however, is more convenient for a polydisperse aggregative system.

Considering the equilibrium between aggregates of various sizes, the values of  $\mu_1$  and  $c_1$  are characteristic constants of the size distribution, and the monomeric concentration  $c_1$  may be taken for a standard concentration. Putting  $c_s = c_1$  in Eq. (16), the mass action law becomes:

$$c_n = K_1 c_1 \quad (20)$$

where  $K_1$  is a new value of the coefficient  $K$  for this particular choice of a standard concentration. The advantage of Eq. (20) is that it is invariant to the way in which the concentrations are expressed. In particular, we may again use molarities in Eq. (20) and, by comparison of Eq. (19) and (20), obtain the relationship:

$$K_1 = K_M c_1^{n-1} \quad (21)$$

For a dilute aggregative system, when  $K_M$  and  $K_1$  are true constants,  $K_M$  is independent of the monomeric concentration and Eq. (21) gives an explicit dependence of  $K_1$  on  $c_1$ . This dependence is more pronounced for larger aggregation numbers.

Evidently, Eq. (19) is equivalent to Eq. (12) with  $W_s = -\ln K_M$  and Eq. (20) is equivalent to Eq. (11) with  $W = -\ln K_1$ , so that  $W$  in Eq. (11) is a standard work. Eq. (21) establishes the relation between these two works as:

$$W = W_s - (n-1) \ln c_1 \quad (22)$$

from which  $W$  is seen to be also dependent on the monomeric concentration. In other words,  $K_1$  in Eq. (20) and  $W$  in Eq. (11) are constant only for a given size distribution at fixed physical conditions. It is seen from Eq. (11) that  $W > 0$  if  $c_n < c_1$ , which is typical for aggregative systems. We may conclude that both Eqs. (11) and (12) are correct and originate from the mass action law, only differing in the choice of standard state. The constant in Eq. (12) is more universal than that in Eq. (11), but the latter is more universal with respect to the choice of concentration units. In addition, Eq. (11) is much simpler in calculations, which has made it so popular in the literature.

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