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Theoretical estimation of the critical packing parameter of amphiphilic self-assembled aggregates

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ABSTRACT

The estimating of critical packing parameter (p) of amphiphilic compounds is considered as a hypothetical rather than an empirical. Consequently, an attempt has been made for determining such a dimensionless parameter for homologous series of sodium *p*-*n*-alkyl benzoates ($n = 0$–8) hydrotropes using quantum mechanical calculations that depend on density functional theory (DFT). The calculations were based on the following well-defined model, $p = v/a_0 l_c$, where v is the volume of the hydrotrope tail, a_0 is the effective head group area and l_c is the length of the extended hydrotrope tail. It was found that the magnitude of both v and l_c parameters can be estimated directly from quantum mechanical calculations. While the investigations found that the a_0 parameter is parallel to the Connolly solvent accessible surface area (C_{sa}) which could also be determined through theoretical computations. The obtained results were in good agreement with published data using small angle neutron scattering (SANS) technique. Hence, the theoretical model for predicting p of amphiphilic at critical micelle- or aggregation-concentration (*cmc* or *cac*) is $p = v/C_{sa} l_c$. An apparent success was observed through applying this simple model to some randomly selected surfactants. It has been concluded that the theoretical calculations that based on quantum mechanical (DFT) method can be considered as a powerful tool for estimating the critical packing parameter of amphiphilic molecules. Finally, the results strongly suggest the employment of the presented model for estimating p of amphiphilic molecules at *cmc* or *cac* by computational chemistry software.

1. Introduction

The geometry of the formed three dimensional aggregates by surfactants is depending merely on concentration and shape of such amphiphilic molecules. This due to the simple geometrical considerations expressed by the surfactant critical packing parameter (p) relation (1):

$$p = \frac{v}{a_0\, l_c} \tag{1}$$

where v is the volume of the hydrotrope tail, a_0 is the effective head group area and l_c is the length of the extended hydrotrope tail as illustrated clearly in Scheme 1. Hence, the aggregation shape of amphiphilic molecules can be speculated according to the value of p For example, when $0 < p \leq 1/3$ only spherical micelles exist in solution. If $1/3 < p \leq 1/2$ aggregations with a rod-like shape or hexagonal are most likely. While, For the value $1/2 < p \leq 1$ there is a balance between sizes of the head group and tail, which causes the surfactant molecule forming planer aggregates with a sheet-like bi-layer structure (i.e. vesicles) [1]. Although, p could be considered as a powerful tool for realizing, rationalizing and predicting the self-assembled structure and its morphological transition in amphiphilic solutions. But, up to now the estimation of such important parameter is regarded as hypothetical rather than empirical. In other words, a state of complexity and speculation is commonly facing researcher who deals with supramolecular aggregate.

According to literature, Tanford [2] and Israelachvili et al. [3,4] introduced appreciable efforts for modeling the proposed combination between molecular structure with size and shape of the resulting self assembled by surfactant molecules. This pioneered work was supported and developed by Nagarajan [5,6]. In addition to several works have been published concerning with this parameter (p) [7–14]. However, no theoretical method has been applied for estimating the packing parameter for amphiphilic molecules except only empirical methods that based on some hypothetical parameters have been found. Indeed, the main problem that faced scientists through determining p is the estimation of a_0 property.

One of our main objectives in this study is to employ quantum mechanical calculations for estimating p of self-assembled amphiphilic molecules. Although, the amount of p is not fixed which depends merely on concentration of these molecules and also on the existence of co-solute in solution [15,16]. In other words, when the surfactant concentration laying at critical micelle

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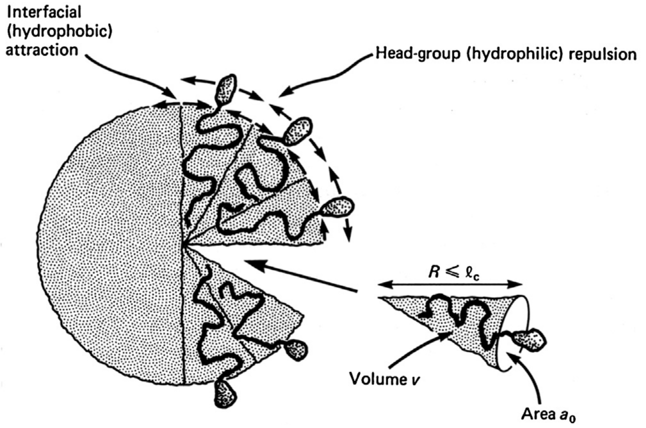


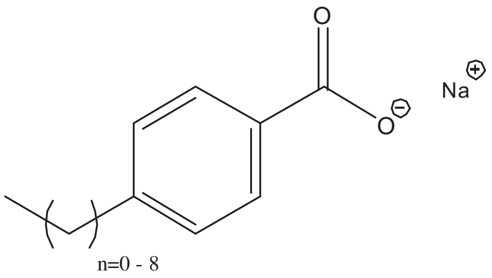
Scheme 1. Visualization of the geometrical consideration for the amphiphilic packing parameter [2].

concentration (*cmc*) the most probable shape of formed micelle is a spherical, as it is well known that the spherical shape possesses lowest area to volume ratio. Therefore, it is not possible to calculate theoretically the packing parameter at concentration over *cmc* due to geometrical transformation of the micelle shape. On the other hand, the presence of co-solute in surfactant solution also could make such geometrical transformation of micelle shape [15,16]. Hence, the theoretical facilities could be utilized for determination p only at *cmc* or *cac* (critical aggregation concentration) for hydrotropes without any foreign compounds in order to forbid the transformation process from spherical shape of aggregate to others. In general, it should be mentioned that it is not logically to obtain a value of p with an absolute precision for dispersion systems. Because the above mentioned model (1) for determining p was hypothetically suggested with regard to fixed geometrical shape of aggregate from engineering point of view not to dynamical structure of micelle [17].

In present investigation, an effort has been made for determining p for homologous series of sodium *p*-*n*-alkyl benzoates (n = 0–8) hydrotropes (Scheme 2) using quantum mechanical calculations based on density functional theory (DFT). Indeed, the use of sodium *p*-*n*-alkyl benzoates (n = 0–8) hydrotropes for the presented investigations gives a fresh opportunity for the possibility of using quantum mechanical calculations for predicting p of amphiphilic molecules. This due to that the shapes of these hydrotropes were already detected as spherical through the results of small angle neutron scattering (SANS) technique by Hatzopoulos et al. [18].

2. Computational details

The chemical structures and their models of sodium *p*-*n*-alkyl benzoates (n = 0–8) hydrotropes were drawn using Hyper Chem program release 8.0.8 for windows operating system. Each structure undergoes stepwise energy minimization starting from molecular mechanics, then semi-empirical PM3 followed with DFT of minimal basis set with Hartree–Fock (HF) exchange without correlation, and finally employing DFT with small (3-21G) basis set and Beck's three parameters hybrid functional, using the correlation function of Lee, Yang and Parr (B3LYP). It has been found that the use of molecular dynamics calculations and conformational search followed by a geometry optimization at small (3-21G) and (B3LYP) are powerful tools to reach the global minima. Details of the computational methodology were briefly illustrated in Refs. [19,20].



Scheme 2. Chemical structure of sodium *p*-*n*-alkylbenzoates.

3. Results and discussion

The use of hydrotropes for estimating p has a significant advantage in contrast to that of ionic surfactants. This can be attributed to the relatively higher ionization constant of polar group of the latter molecules in contrast to that of hydrotropes. Indeed, the decrease in ionization constant has a direct effect on lowering the probability of forming free gegen-ions. In other words, the absence of free gegen-ions at Gouy–Ghapman layer making the distribution of amphiphilic molecules more ordered which therefore the spherical aggregates becomes relatively more symmetrical. Such status will makes the theoretical calculations very adequate as each one molecule will represents all the aggregated molecules in supramolecular structure. Furthermore, aggregation shape at *cac* of the used hydrotropes (sodium *p*-*n*-alkyl benzoates; n = 0–8) in this work is already well-known as spherical through the results of small angle neutron scattering (SANS) technique by Hatzopoulos et al. [18], indicating all of these hydrotropes behave as surfactant like. Actually, the presented work may also give support to this phenomenon.

Whatever, in order to estimate p according to Eq. (1) using DFT calculations one must first evaluate v, a_0 and l_c parameters. The volume of hydrophobic tail (v) has been directly estimated from QSAR calculations facility that already exist in Hyper Chem software (Table 1). In a similar manner, the hydrophobic chain length (l_c) has also been calculated as listed in Table 1. But, the bottle neck was found through determining the effective surface area per polar head (a_0). Such problem was already faced the scientists who dealing with this criterion [2–6,13]. Thus, there is no hint or direct method for calculating this property using computational software, which therefore, considerable efforts must be taken in order to sort out this problem theoretically. Consequently, several methods were suggested here in order to estimate a_0 parameter. The first attempt was carried out through drawing two hydrotropes molecules using Hyper Chem software. Then, the distance between the heads of these two molecules has been estimated according to the minimized energy of DFT method. Such distance (5.2 Å) can be considered as a diameter which then divided by 2 in order to find the radius of head group as illustrated in Fig. 1. However, the p values that calculated using this suggested method (method 1, M1) are not reasonable because these values are quite far from the range of common critical packing parameter values as illustrated in Table 1. The reason for such non practical values may be attributed to presence of solvent molecules (H_2O) between head groups. Indeed, the presence of solvent molecules is more likely from energy point of view in order to decrease the electrostatic repulsion between head groups.

The second attempt (method 2, M2) was carried out through taking the polar surface of hydrotrope under account. Thus, in a similar manner of method 1, two optimized molecules were drawn in order to measure the distance between the polar surfaces of the head group of those molecules as elucidated in Fig. 2 (6.4 Å). Again, no reasonable results were found using M2 as seen clearly in Table 1.

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