Prediction of Surfactants' Properties using Multiscale Molecular Modeling Tools: A Review

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Résumé — **Prédiction de propriétés des tensioactifs à l'aide d'outils de modélisation moléculaire : une revue** — Une des voies possibles de récupération assistée du pétrole, l'EOR (*Enhanced Oil Recovery*), consiste en l'injection d'un fluide ASP (*Alkaline/Surfactant/Polymer*) dans le réservoir dans le but de déplacer le pétrole piégé vers le puits de production. La conception et/ou l'optimisation de mélanges ASP, de tensioactifs ou de mélanges de tensioactifs est donc d'un intérêt premier pour améliorer l'efficacité d'un tel procédé. Les codes de simulation moléculaire développés et largement validés durant ces dernières décennies apparaissent comme des outils incontournables pour la compréhension des effets microscopiques, la prédiction de propriétés de tensioactifs complexes ou encore l'optimisation des structures voire de la composition de mélanges de tensioactifs. Dans cet article, nous présentons une revue des travaux de la littérature sur le potentiel de diverses techniques de simulation moléculaire pour la prédiction de propriétés structurales ou thermophysiques des tensioactifs. Les techniques de simulation auxquelles nous nous sommes intéressés sont la dynamique moléculaire (MD), les simulations Monte Carlo (MC), la *dissipative particle dynamics* (DPD) ainsi que des approches statistiques faisant un lien direct entre structure et propriété (QSPR, pour *Quantitative Structure-Property Relationship*).

Abstract — *Prediction of Surfactants' Properties using Multiscale Molecular Modeling Tools: A Review* — *During one of the existing Enhanced Oil Recovery (EOR) procedures, a mixture of Alkaline/Surfactant/Polymer (ASP) is injected into wells in order to move the trapped oil from the reservoir to the wellbores. The conception and/or the tuning of new ASP combinations, structures of surfactants and/or mixtures of surfactants is of primary interest to improve the efficiency of a such procedure. Molecular modeling tools can be used to understand microscopic effects, predict surfactants' properties and finally to optimize structures and mixtures of surfactants. We propose in this article a review of the literature on the ability of molecular simulation techniques such as Molecular Dynamics (MD), Monte Carlo (MC) simulations, Dissipative Particle Dynamics (DPD) and upper scale modeling methods such as Quantitative Structure-Property Relationship (QSPR) approaches to predict thermo-physical and structural properties of surfactants.*

SYMBOLS AND ACRONYMS

ANFIS	Adaptive Neuro-Fuzzy Inference System
ANN	Artificial Neural Networks
ASP	Alkaline/Surfactant/Polymer
CG	Coarse Grained
CMC	Critical Micelle Concentration
CTAB	Cetyltrimethylammonium bromide
DFT	Density Functional Theory
DPD	Dissipative Particle Dynamics
EOR	Enhanced Oil Recovery
F	Fisher test value
FFS	Forward Flux Sampling
GCMC	Grand Canonical Monte Carlo
GFA	Genetic Function Approximation
H	Head groups in a surfactant
HLB	Hydrophile-Lipophile Balance
HRM	Histogram Reweighting Method
IFT	Interfacial/surface Tension
MC	Monte Carlo
MD	Molecular Dynamics
MLR	Multiple Linear Regression
PLS	Partial Least Squares
QSPR	Quantitative Structure-Property Relationship
R^2	Coefficient of determination
S^2	Standard error
SCFT	Self-Consistent Field Theory
SCMF	Single Chain Main-Field
SDS	Sodium DodecylSulfate
SGMC	Semi-Grand Canonical Monte Carlo
SHS	Sodium HexylSulfate
SVM	Support Vector Machines
T	Tail groups in a surfactant
TA	Test Area
WIM	Wandering Interface Method

INTRODUCTION

The actual capacity of oil extraction still remains limited and can be roughly estimated to 30-60%, or more, of the reservoir's original oil within the considered field [1]. The production process is typically split into tree distinct phases:

– the primary recovery which is the consequence of natural effects such as the pressure of the reservoir;

– the secondary recovery which consists in injecting water or gas to move the oil to the wellbore;

– the tertiary recovery or Enhanced Oil Recovery (EOR), which gathers techniques such as thermal recovery, chemical or microbial injection [2-4].

The chemical injection technique can involve combinations of Alkaline/Surfactant/Polymer (ASP) in which the alkali reacts with some of the crude oil components decreasing the water/oil InterFacial/surface Tension (IFT) [5]. Surfactants are used to reduce the water/oil IFT and the role of
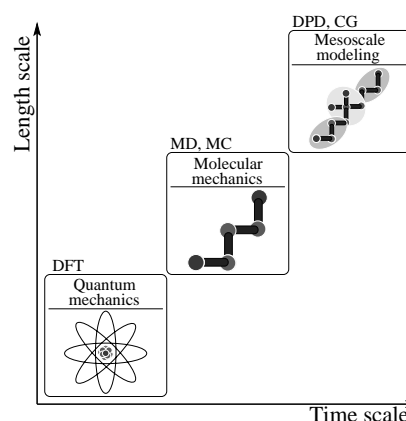

Figure 1

Multiscale molecular modeling tools from quantum mechanics to mesoscale modeling.

the polymer is to improve the sweep efficiency. Although this technique suffers from its relatively high cost mainly due to injected chemicals' cost, it becomes economically viable when crude oil prices increase.

The optimization of the ASP combination to reservoir's characteristics such as the salinity, the temperature or the type of rocks appears of primary interest when attempting to maximize the rate of oil recovery. This optimization should profit from the systematic use of molecular modeling tools developped and optimized during the last decades. Indeed, in combination with recently developed intermolecular potentials, molecular modeling tools can provide precise information about microscopic phenomena and lead to acurate estimation of thermophysical properties [6-10]. Figure 1 schematically represents the main simulation techniques used to describe the matter from an atomistic to a mesoscale level. The information that can be extracted using these techniques vary from the level of approximation, *e.g.* the explicit electronic description of atoms is lost when using methods such as Molecular Dynamics (MD), Monte Carlo (MC) or Dissipative Particle Dynamics (DPD). Furthermore, during last decades a large number of studies has been devoted to statistically link structure and properties of molecules through so called Quantitative Structure-Property Relationship (QSPR) approaches [11]. The development of an *in silico* screening procedure combining cited methods could guide and improve the efficiency of the selection of optimal surfactants or mixtures of surfactants compared with the actual required experiments [12]. An overview of the literature content regarding applications of simulation techniques to compute properties of surfactants is the first step of such a tool development.

Surfactants are amphiphilic molecules, it means they contain both nonpolar groups ("tail'', labelled T) and polar

groups ("head'', labelled H). These two substructural features indicate these compounds are both oil and water soluble. The ratio of a surfactant hydropilicity to its hydrophobicity defines the Hydrophile-Lipophile Balance (HLB) which mainly spreads in the range 0 to 40 indicating affinity with water and oil, respectively. HLB is a tool developed to classify surface active agents, widely used to quantify physicochemical formulations of surfactant/water/oil systems (whatever the industrial field). At low concentration, surfactant molecules exist as individual entities and are preferentiallly located at the water/oil interface. The addition of surfactants in a water/oil system causes the IFT decreasing. Regarding EOR applications, IFT deals with elementary physico-chemical values used to understand and optimize ASP/SP processes. When the concentration of surfactants increase, surfactants aggregate and form micelles having a spherical shape. The concentration at which spherical micelles occur is called the Critical Micelle Concentration (CMC). Thus, CMC values of surfactants are used in EOR applications to indicate whether the surfactant molecules are aggregated or not. For some surfactants and concentration above the CMC, micelles can evolve from spherical to cylindrical shapes, the concentration at which this phenomenon occurs defines the second CMC.

The paper which is devoted to the prediction of surfactant properties using molecular modeling tools is organized as follows: in Section 1, we present how the use of techniques such as MD and MC can lead to the prediction of IFT and CMC; in Section 2, studies devoted to surfactants' properties using the DPD technique are presented; and in Section 3, QSPR type models developed to predict CMC, IFT and HLB of surfactants are listed and commented. This paper ends with the conclusions and perspectives.

1 MOLECULAR DYNAMICS AND MONTE CARLO SIMULATIONS

During the two last decades, complex systems containing surfactants have been studied using molecular modeling methods such as MD or MC. Although the computational power has been increased using massive parallelized codes, the simulation of the aggregation process of surfactants is still a challenging task. An appropriate choice between a continuous and detailed description of the space [13-17], and the use of a lattice model with approximative descriptions of solvent/surfactant molecule interactions is still required [18-23]. One of the key tasks is the phase diagram computation of systems containing surfactants. As there is no evident phase transition between isolated surfactants and micelles, the CMC value mainly depends on the definition used. The most common one defines the CMC as the concentration where the number of aggregated surfactants is half the total number of surfactants [24].
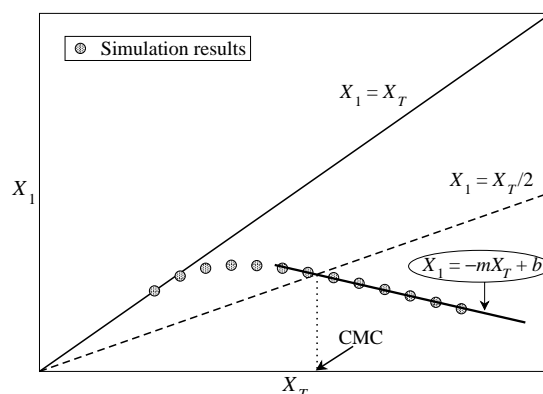

Figure 2

Schematic representation of the evolution of the isolated surfactants concentration (X_1) as a function of the total concentration of surfactants (X_T).

1.1 CMC Calculation

The CMC determination using molecular simulation tools needs the computation of $P(N)$, the aggregation probability of N molecules However, the minimum number of surfactants required to form a micelle is system dependent. For instance, Sammalkorpi *et al.* [25] placed this limit at 7 molecules. It appears wiser to adjust $P(N)$ to an analytical Γ function according to:

$$P(N) = \left(\frac{1}{\beta} C_r \Gamma(\alpha)\right) N^{\alpha-1} e^{(-N/\beta)} \quad (1)$$

where α, β and C_r are three adjustable parameters. The concentration of isolated surfactants is defined as follows:

$$C^{CMC} = \frac{n_s}{V} \sum_{N=1}^{6} (N \cdot P(N)) \quad (2)$$

where n_s is the total number of surfactants and V is the volume of the system. The two weak points of this method lies in the fact that the maximal size of the micelle is arbitrary and in the numerical criteria to determine $P(N)$.

The CMC is also graphically accessible by representing the concentration of isolated surfactants, (X_1), as a function of the total concentration of surfactants, (X_T), see Figure 2. Considering that above the CMC, $X_1 = f(X_T)$ is a decreasing linear function, the CMC can be defined as the intersection of $X_1 = -mX_T + b$ and $X_1 = X_T/2$ functions.

There are several works in the literature where MC simulations have been performed in order to study surfactants' aggregation and structure, as well as CMC calculation [14, 22, 26-32]. For instance, Talsania *et al.* [26] have used lattice Monte Carlo to explore the formation and stabilization of micelles with contaminants. Later, Talsania *et al.* [27] have reproduced phase diagrams of

surfactant/solute/solvent systems and studied the impact of the hydrophobicity and the size of the solute. In 1997, Mackie *et al.* [28] have compared the structure of micelles and CMC computed using Monte Carlo simulations with theoretical predictions based on the Single Chain Main-Field (SCMF) theory. The *in silico* formation of micelles was studied by Floriano *et al.* [14] by the mean of Grand Canonical MC (GCMC) simulations combined with the Histogram Reweighting Method (HRM). In this work, authors have shown an important variation of the osmotic pressure around the CMC at low temperatures. In a similar way, Pool and Bolhuis [29] have studied using Semi-Grand Canonical Monte Carlo (SGMC) simulations of the free energy of the formation of micelles for different surfactants in a Lennard-Jones type solvent and computed CMC values in agreement with experimental data. One can remark that this methodology has been used again by Cavallo *et al.* [30] and applied to the study of polymer aggregation. Futhermore, Gharibi *et al.* [31] have shown that the addition of a macromolecule such as a polymer have two consequences:

– the decrease of the CMC value;

– micelles having a more spherical shape compared with systems without macromolecule, in agreement with theoretical and experimental results.

Lísal *et al.* [22] have performed MC simulations of surfactant/solvent systems where the solvent is the supercritical CO_2. Two structures of surfactants were studied H_4T_7 and H_4T_{11}, and several concentrations of surfactants were considered. The analysis of the CMC for both surfactants of interest have shown intervals where spherical, elongated or egg-shape micelles occur in supercritical CO_2. One can also mentionned the works of Hashemianzadeh *et al.* [32] in which ionic surfactants have been modeled and electrostatic interaction were included in the lattice model.

Molecular Dynamics simulations have been also used to study and predict aggregation, structure and the CMC of surfactants [25, 33-38, 40, 41]. Jorge [33] and Stephenson *et al.* [34-36] have performed MD simulations to mimic the aggregation processus of ionic and nonionic surfactants in water. Simulations results have revealed a three-stage evolution of micelles, *i.e.* monomer aggregation to form oligomers, growing of oligomers and collisions between micelles. Recently, MD simulations have been done to study the CMC variations with the addition of salts such as NaCl and $CaCl_2$, for ionic surfactants such as sodium hexylsulfate (SHS) [25]. Particules size distribution and CMC values agree with experimental data. The excess of $CaCl_2$ modifies the structure and properties of micelles, while excess of NaCl does not drasticaly modify those properties. Simulations have also revealed micelles with ovoidal shapes at high concentrations of Sodium DodecylSulfate (SDS). Samanta *et al.* [37] have employed MD simulations to study aggregation properties of multi-head surfactants. Authors have considered various HLB by adding hydrophilic groups

in surfactants, the computed variations of the CMC and size of micelles agree with experimental observations. Maiti *et al.* [38] have developed a CG approach to model dimer (also called gemini) and trimer of surfactants using MD simulations observing the formation of a second CMC. The CG model developed by Marrink *et al.* [39] has been used by Burov *et al.* [40] and Sanders *et al.* [41] to compute the CMC of ionic and zwitterionic surfactants, respectively, through Equations (1) and (2).

1.2 IFT Calculation

The most common methods to compute of the IFT using molecular simulations are based on mechanical laws through pressure tensor calculation. The definition of IFT given by Kirkwood and Buff, γ_{KB}, is presented in Equation (3) [42]:

$$\gamma_{KB} = \frac{L_z}{2}(P_N - P_T)$$
$$= \frac{1}{2A}\left\langle \sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\frac{r_{ij}r_{ij} - 3z_{ij}z_{ij}}{2r_{ij}}\frac{dU(r_{ij})}{dr_{ij}}\right\rangle \quad (3)$$

where, L_z is the size of the simulation box along the *z*-axis, P_N and P_T are the normal and tangential components of the pressure tensor, respectively, *A* denotes the area between surfaces, z_{ij} is the *z*-axis component of the r_{ij} distance and *U* represents the intermolecular potential. Nevertheless, when systems with heterogenous densities are considered the long-range corrections approximated as constant are no longer valid. Blokhuis *et al.* [43] have developed specific long-ranged corrections based on the radial distribution function and the density profile fit using an hyperbolic function.

Irving and Kirkwood [44] have proposed a definition of the IFT based on the local components of the pressure tensor, as expressed in Equation (4):

$$\gamma_{IK} = \frac{1}{2}\int_0^{L_z}(P_N(z) - P_T(z))\,dz \quad (4)$$

In 1997, Guo and Lu [45] have developed long-ranged corrections used in molecular simulation for internal energy, pressure and IFT without any hypothesis on the density profile. In 2006, Janeček *et al.* [46] have proposed a modification of Guo and Lu long-ranged corrections but using a dependence with the local density profile. More recently, MacDowell and Blas [47] proposed a modification of Janeček *et al.*'s long-ranged corrections without any hypothesis on the density profile.

Under certain thermodynamic considerations, the interfacial tension can be expressed as the derivative of the system free energy with respect to the surface area. Some methods such as WIM (Wandering Interface Method) and TA (Test Area) are based on these thermodynamic considerations [48, 49]. For instance, TA consists in perturbing

the surface area of the interface and to deduce the IFT value from the associated free energy variation.

Molecular simulations have been used to study and predict interfacial tension of pure components and mixtures, hereafter we focus on applications related to properties of surfactant/water/hydrocarbon systems. Jang *et al.* [50] have studied the behavior of surfactants such as sulfonate alkylbenzen in oil and the impact of the branching on the IFT. Using molecular simulations, Ma *et al.* [51] have shown that surfactants such as the SDS decrease the IFT at water/air interface. Stephenson and Beers [52] have performed molecular dynamics simulations at fixed IFT for various surfactants at water/air interface. Authors discussed several properties such as the mean surface of surfactants at the interface, the evolution of this surface with the IFT, or density profile. In 1997, Urbina-Villalba *et al.* [53] have used MD simulations to study the variation of surface energy and entropy of the *n*-heptane/water system for different temperatures and different concentrations of surfactants. Three simulation boxes: one with the surfactant, one with *n*-heptane and one with water, were studied separately and energies of each simulation box were injected in a theoretical model in order to link the molecular structure with the IFT. In 2002, Da Rocha *et al.* [15] have studied the behavior of an anionic surfactant at an H_2O/CO_2 interface. In a similar way, Stone *et al.* [16] have studied how fluorohydrocarbon may stabilize an H_2O/CO_2 interface.

1.3 Winsor I-II-III Transition

The number of phases in a surfactant/brine/hydrocarbon system depends upon the temperature, the surfactant concentration and/or the salinity. The variation of these factors induces phase transition known as the Winsor transition. The Winsor I $\rightarrow$ III $\rightarrow$ II transition is illustrated in Figure 3. Behjatmanesh-Ardakani and Nikfetrat [54] have used Monte Carlo simulations to qualitatively study the influence of the temperature, the size of *H* and *T* of surfactants and the oil on these types of transition. Authors have shown that the IFT between the oil and the water, γ_{OW}, is related to the lattice energy and simulation results have shown that the γ_{OW} of Winsor III is qualitatively similar to experimental data. The structure modification between Winsor III $\rightarrow$ I (or Winsor II) presents an increase of γ_{OW} in agreement with experimental results.

2 DISSIPATIVE PARTICLE DYNAMICS SIMULATIONS

In the previous section, we have shown that the length and time scales address by molecular simulations such as MC and MD could be increased using a coarse grained description of compounds [39]. This higher level is also accessible through dissipative particle dynamics which is in some way a coarse grained type molecular simulation technique. This
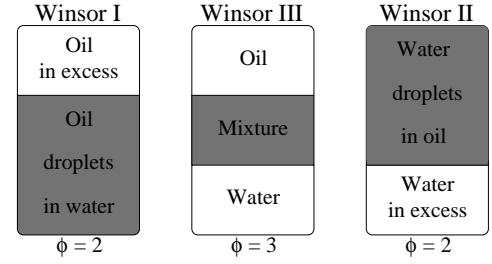
Figure 3

Winsor I $\rightarrow$ III $\rightarrow$ II transition for a surfactant/water/oil system. ϕ is the number of phases.

method was introduced by Hoogerbrugge and Koelman [55] in 1992 and the technique was fully described by Groot and Warren [56] in 1997. While the bases of the DPD are similar to those of MD, *i.e.* the resolution of the equations of motion, in DPD, forces applied on bead *i* can be summurized as follows:

$$f_i = \sum_{j \neq i} \left(F_{ij}^C + F_{ij}^D + F_{ij}^R \right) \tag{5}$$

where F_{ij}^C, F_{ij}^D, F_{ij}^R are the conservative, dissipative and random forces, respectively. To render anisotropy, some authors have linked beads together using bonding (F_{ij}^{Bo}) and bending (F_{ij}^{Be}) forces [57].

2.1 CMC Calculation

In 2006, Pool and Bolhuis [58] attempted to predict the CMC of surfactants using DPD simulations and a Lennard-Jones type model. Authors have shown that the CMC can be estimated with the Lennard-Jones type model with a good agreement with respect to experimental data and that DPD can only provide qualitative predictions of phase behavior. Li and Dormidontova [59] have studied the micellization kinetics of dibloc copolymer molecules and shown predicted CMC values, aggregation number and structures in agreement with experimental data. The micellization time evolution is shown to follow three steps:

– monomer consumption;

– micelles number equilibration;

– small exchanges between micelles.

2.2 IFT Calculation

As presented in Equation (4), IFT can be computed integrating the difference between the normal and tangential pressures. In the case of droplet, Dzwinel and Yuen [60] have computed the IFT, γ_L, using the Laplace law as presented in Equation (6)

$$\frac{2}{R}\gamma_L = P_d - P_c \tag{6}$$

where R is the droplet's radius, and P_d and P_c are the pressures in the disperse and continous phases, respectively. Recently, Ghoufi and Malfreyt [61] have developed a local pressure component formulation for the surface tension of spherical interfaces.

Rekvig *et al.* [62, 63] have used DPD simulations to predict IFT for different surfactant concentrations and the evolution of the IFT of water/oil systems with the branching of surfactants. Maiti and McGrother [64] have compared results obtained using DPD simulations with experimental data for water/oil systems. Simulated results are in agreement with experimental data. More recently, Ginzburg *et al.* [65] have simulated IFT using DPD and Self-Consistent Field Theory (SCFT) for a water/oil/nonionic surfactants with a reasonable agreement with respect to experimental data. Recently, Li *et al.* [66] have studied oil/water systems with the CTAB surfactant and discussed surface tension and mechanical interfacial properties.

2.3 Structure of Surfactants

Li *et al.* [67] as well as Moeendarbary *et al.* [9,10] have published reviews in which they present some of studies dealing with the use of the DPD for the theoretical study of the spatial arrangement of amphiphilic molecules in a solvent, *e.g.* phase characterization, adsorption at the liquid/liquid interfaces, behavior under flow, etc. In 1999, Jury *et al.* [68] have performed DPD simulations for rigid dimers in continous phase of monomers. Later, Ryjkina *et al.* [69] have reproduced the experimental phase behavior of the dodecyldimethylamine oxide. In a similar way, Yang *et al.* [70] have studied the phase organization of an anionic surfactant in water. In the works of Illya *et al.* [71] mechanical properties of bilayers of amphiphilic molecules H_xT_y are investigated using DPD. Shillcock and Lipowsky [72] have studied complex fluids such as bilayers of molecules, membranes, vesicles by the mean of DPD simulations. Zhong and Liu [73] have also studied complex micelles which could be employed for metamaterials synthesis.

Regarding surfactant/water/hydrocarbon ternary systems, Schulz *et al.* [74] have studied using DPD for the phase diagram of a nonionic ethoxylate surfactant, $C_{10}E_4$, in water and in *n*-octane. Authors have reproduced the conformation changes, transition between a bicontinous structure and a L3 phase, with the increase of the surfactant concentration. Rekvig and Frenkel [57] and Rekvig *et al.* [75] have studied oil/water interfaces with surfactants adsorbed. For the nonionic surfactants chosen, the repulsion is mainly steric and entropic. Studying repulsion forces between oil/water/oil films for a given structure of the surfactant, authors are able to recover Bancroft's law stating that an emulsion is stabilized if surfactant is made soluble in the continuous phase [75]. Rekvig and Frenkel [57] have also worked in 2007 on the influence of the morphology of the surfactants on the coalescence in water/oil/surfactants systems.

DPD simulations associated with a Forward Flux Sampling (FFS) method have allowed to follow the evolution of holes in films. It was shown that surfactants with a positive curvature permit a better stabilization of the water film, *i.e.* the oil in water emulsion compared to surfactants with a negative curvature.

In the following, we deal with surfactants interacting with other species such as polymers, cosurfactants, etc., such systems being of great interest for industrial applications. In 2000, Groot [76] has studied a system containing a solvent, a polymer and a surfactant. The end-to-end distance of the polymer is shown to evolve with surfactant concentration: at low concentrations, the end-to-end distance decreases and then increases for concentrations above the CMC. Different numerical simulations approaches concerning the structure of surfactant and polymer are part of a review by Li *et al.* [67]. In 2001, Groot and Rabone [77] obtained results on damage to cell membranes due to nonionic surfactants (C_9E_8, $C_{10}E_8$, $C_{12}E_6$) and compared their effects. Cosurfactants (*e.g.* alcohols with small chain) are very interesting to obtain stable microemulsions when added to water, oil and surfactants systems. Such systems have been studied by Chen *et al.* [78] who have shown that DPD simulations could match experimental phase diagram of a system cetyltrimethylammonium bromide (CTAB)/1-butanol/octane/water. In principle, DPD do not treat long range interactions such as electrostatic ones. However electrostatic interactions may explain the organisation of a lot of systems and most part of ionic (charged) surfactants are concerned. Thus, different ways to implement electrostatics in DPD can be found in the literature. Direct resolution of the electrostatic field on a grid was proposed by Groot [79] and gave results on the interactions between charged polyelectrolytes and surfactants. Ewald method is an other way of calculation shown by Gonzalez *et al.* [80], also used by Ibergay *et al.* [81, 82] for polyelectrolytes.

3 QUANTITATIVE STRUCTURE-PROPERTY RELATIONSHIPS

The main objective of QSPR methodologies is to relate features of molecules (molecular descriptors) with experimental values of a property. It is important to mention that the development of a QSPR model must be done with great care, and the following paragraph provide some of the key points [11, 83]. The keystones for the accuracy of a predictive model are first the size and quality of the database and second the calculation of relevant descriptors. Compounds in the database must be representative of chemical families targeted in the study. Property values can be gathered from experimental measurements, chemical databases or from the literature as long as they are self-consistent to limit the statistical noise in the database. Molecular structures of compounds in the database are

drawn and geometries have to be optimized through the same procedure. A large number of molecular descriptors exists and have already been successfully used in correlative models. Most of the time descriptors are properties or constants of molecules or derived from empirical formula, structural formula or spatial representation of molecules. Descriptor combinations can also be done. The database is split into two data subsets:

– the training set which is chosen to be representative of the chemistry and the range of property values in the database, is intended to the learning stage of the predictive model;

– the test set is made up with the remaining molecules of the database and these latter molecules are viewed as external compounds and used to test the predictive power of models.

Varied techniques have been developed to select the most relevant descriptors and to relate them with the target property through linear models such as Multilinear Regression (MLR), Partial Least Squares (PLS) or non-linear models such as Artificial Neural Networks (ANN), Support Vector Machines (SVM), etc. For instance, the calculated property value $P_{calc.}$ can be written as follows when modelled using a multilinear model:

$$P_{calc.} = \lambda_0 + \sum_{i=1}^{n} \lambda_i X_i \tag{7}$$

where λ_i and X_i denote coefficients and descriptors, respectively. Accuracy of correlative models can be expressed through various statistical coefficients such as the standard error S^2, the Fisher test value F or the well-known coefficient of determination, R^2 as defined in Equation (8) [84]:

$$R^2 = \frac{\sum_{i=1}^{n}(P_{calc.,i} - \langle P \rangle)^2}{\sum_{i=1}^{n}(P_{exp.,i} - \langle P \rangle)^2} \tag{8}$$

where i runs over the n compounds in the data set, $P_{calc.}$, $P_{exp.}$ and $\langle P \rangle$ denote calculated, experimental and mean of experimental property values, respectively.

Katritzki *et al.* [11] as well as Hu *et al.* [85] have published reviews in which they present some studies dealing with the use of QSPR for the modeling of surfactant properties. Part of the information contained in both of these reviews has been taken up and completed to build the sections hereafter.

3.1 CMC Prediction

The challenge of the theoretical determination of the CMC has been starting since about 40 years. The first attempt was performed by Rosen [86] who proposed a two terms equation, similarly a three terms equation was published

TABLE 1

Statistical coefficients of QSPR models intended to the prediction of the critical micelle concentration. n is the total number of compounds used in the database, $\bigcirc$, $\oplus$ and $\ominus$ stand for nonionic, cationic and anionic surfactants, respectively

	QSPR	n	R^2	F	S^2	Ref.
$\bigcirc$	MLR	23	0.980	1 042	–	[97]
	MLR	39	0.995	–	0.123	[92]
	MLR	45	0.990	803	–	[93]
	MLR	50	0.989	391	0.236	[95]
	MLR	54	0.907	–	–	[98]
	MLR	77	0.984	1 433	0.031	[89]
	MLR	77	0.903	131	–	[94]
	MLR	162	0.888	310	0.203	[96]
	ANN	162	0.946	–	0.309	[96]
$\oplus$	MLR	23	0.993	1 477	0.102	[101]
	MLR	30	0.954	69	0.220	[99]
	MLR	50	0.977	380	0.019	[100]
	ANN	50	0.974	–	–	[100]
$\ominus$	MLR	31	0.996	477	0.066	[102]
	MLR	37	0.996	1 839	–	[103]
	MLR	98	0.980	1 505	0.011	[105]
	MLR	119	0.940	597	0.047	[90]
	MLR	119	0.871	–	–	[94]
	MLR	133	0.976	5 360	0.014	[104]
	PLS	175	0.951	562	0.040	[107]
	MLR	181	0.926	412	0.058	[106]

by Becher [87] in 1984 and finally Ravey *et al.* [88] proposed to add a nonlinear term to improve Becher's equation (*see Eq. 9*):

$$\log CMC = A + Bn + Cm + Dnm \tag{9}$$

where n denotes the number of carbon atoms, m the ethylene oxide number, $A = 1.77$, $B = -0.52$, $C = 0.032$ and $D = 0.002$.

During the last decades, the number of published QSPR studies have hugely increased, mainly due to the evolution of the computational power and to the development of powerfull statistical approaches and softwares. The first QSPR models for the prediction of the CMC were reported by Huibers *et al.* who proposed equations for nonionic [89] and anionic [90] surfactants. Both of these QSPR models were obtained using MLR approach over a set of descriptors based on molecular topology and constitution. Apart from the work of Anoune *et al.* [91], QSPR models intended to the CMC prediction were trained over specific chemical families that are: nonionic [89, 92-98], cationic [99-101], and anionic [90, 94, 102-107] surfactants. Table 1 presents statistical coefficients of QSPR models listed in the literature. This table shows that most of these models have been developed using MLR and we can remark that the size of the database varied from few tens to less than two hundred compounds. Katritzky [96] and Katritzky *et al.* [100, 106] have published the QSPR models for the CMC learned using

the most comprehensive databases. In these two last works, authors present comparisons between MLR and ANN models. For nonionic surfactants [96], the ANN model is reported to perform better than the four-descriptor based MLR. In the case of cationic surfactants [100], the five-descriptor multilinear model developed by Katritzky *et al.* shows comparable performance with respect to that of the ANN model. Katritzky *et al.* stated that their models are reliable tools and consequently will be used to predict CMC of similar surfactants. Note that some QSPR models have also been developed for the prediction of the CMC of gemini surfactants [108-110]. Bhhatarai and Gramatica [111] have recently developed two MLR models for the prediction of the CMC of perfluorinated chemicals, based on connectivity indices and C-F bond numbers, respectively. The authors have not split the database since it only contains 10 compounds, reported statistical coefficients for these two models are: $R^2 = 0.973$, $F = 293$, and $R^2 = 0.936$, $F = 117$.

3.2 IFT Prediction

Very few works have been published regarding the development of QSPR models for the prediction of the interfacial tension, γ, of surfactants. Wang *et al.* [112-114] who are the main contributors in this area, have developed a first QSPR model using a database including experimental interfacial tension values at the CMC, γ^0, for 30 nonionic surfactants [112]. The two-descriptor based model can be formulated as follows:

$$\gamma^0_{pred.} = 12.66 - 0.01529 \times \Delta H_f + 0.6310 \times KHO \\ + 0.0006576 \times \Delta H_f.KHO \qquad (10)$$

where ΔH_f and KHO denotes the heat of formation and a topological descriptor, respectively. Authors returned an $R^2 = 0.976$ for Equation (10). In 2005, Wang *et al.* [114] have proposed a new model using the same database and new descriptors such as the number of oxygen atoms (NO) in the hydrophile group, E_T the total energy and D the dipolar moment. For the resulting model which is given by Equation (11), authors reported the following statistical coefficients: $R^2 = 0.994$, $F = 188$ and $S^2 = 0.530$.

$$\gamma^0_{pred.} = 11.98 - 0.01053 \times \Delta H_f + 0.5848 \times KHO \\ + 0.09734 \times D + 0.4780 \times NO \qquad (11) \\ - 0.0007763 \times E_T + 0.1345 \times NO.KHO$$

Wang *et al.* [113] have also investigated the prediction of γ^0 for anionic surfactants using a database which consits of 34 experimental values measured for 20 anionic surfactants at different temperatures, T. Authors proposed a five-descriptor model including ΔH_f, D, KHO and C the counter ion concentration and which accounts for the temperature dependence of the property. The returned statistical coefficients of Equation (12) are the following: $R^2 = 0.988$,

TABLE 2

Statistical coefficients of QSPR models intended to the prediction of the interfacial tension. *n* is the total number of compounds used in databases

QSPR	n	R^2	F	S^2	Ref.
MLR	68[a]	0.986	845	0.200	[116]
MLR	68[a]	0.989	1 152	0.200	[116]
MLR	166[b]	0.983	–	0.400	[117, 118]
MLR	68[a]	0.976	–	–	[119]
MLR	199[b]	0.863	–	–	[121]
MLR	68[a]	0.959	199	0.410	[122]
MLR	320[b]	0.960	1 317	1.430	[123]
MLR	196[b]	0.783	–	–	[124]
SVM	196[b]	0.931	–	–	[124]
GFA	142[c]	0.980	–	–	[125]
ANFIS	142[c]	0.985	–	–	[125]
ANN	752[b]	0.997	–	0.020	[126]
ANN	1 604[b]	0.985	–	0.010	[127]

[a] alkanes, [b] organic compounds and [c] alcohols.

$F = 56$ and $S^2 = 0.013$ and, since biases (shift and rotation) were observed between $\gamma^0_{pred.}$ and $\gamma^0_{exp.}$ the authors proposed the use of the regression Equation (13) leading to $R^2 = 0.994$ and $S^2 = 0.07$. Very recently, after performing experimental measurements on 24 ionic surfactants Fini *et al.* [115] have developed a multilinear model for the prediction of the *n*-decane/water IFT. Authors report the following statistical coefficients: $R^2 = 0.930$, $F = 83$, and $S^2 = 0.07$:

$$\gamma^0_{pred.} = 27.71 - 0.005239 \times \Delta H_f + 1.080 \times KHO \\ - 0.2130 \times D + 17.16 \times C \qquad (12) \\ - 0.1520 \times T$$

$$\gamma^0_{pred.} = 2.982 + 0.9199 \times \gamma^0_{exp.} \qquad (13)$$

A large number of works dealing with the development of QSPR models for the prediction of the interfacial tension for other chemical families has been reported in the litterature [116-127]. These works are summurized in Table 2. Since the beginning of the 90s, the size of databases used for the development of models has increased and non-linear methods seem to be preferred in the most recent studies. In their last study, Gharagheizi *et al.* [127], have developed an ANN which accounts for the temperature dependency of the interfacial tension, using a database containing 18 298 data belonging to experimental interfacial tension values of 1 604 compounds at different temperatures. 20 descriptors including the temperature and descriptors based on molecular topology and constitution such as the numbers of multiple bonds, of primary alcohols, etc., were identified as most relevant for this study. The ANN was trained over a test set which consists of 14 640 interfacial tension data. Coefficients of determination $R^2 = 0.985$ were reported by authors for both the training and test sets revealing a good ability of the model to predict IFT and showing that there is no overfitting of the data.

TABLE 3

Statistical coefficients of QSPR models intended to the prediction of the HLB. n is the total number of compounds used in the database and ◯ and ⊖ stand for nonionic and anionic surfactants, respectively

	QSPR	n	R^2	F	S^2	Ref.
◯	MLR	39	0.982	1 031	1.052	[133]
	MLR	90	0.984	629	0.476	[132]
⊖	MLR	46	1.000	130 259	0.003	[131]
	MLR	73	0.996	1 781	0.015	[131]
	MLR	65	0.970	113	3.232	[134]
	MLR	73	0.981	3 729	–	[135]
	ANN	73	0.996	17 323	–	[135]

3.3 HLB Prediction

Since the end of the fifties, the HLB of surfactants can be estimated using Equation (14), the Davies' group contribution method [128]:

$$\text{HLB} = 7 + \sum (\text{hydrophilic group contribution})$$
$$- \sum (\text{lipophilic group contribution}) \quad (14)$$

where, for instance, the last term represents the sum of products of group number times the value associated to the group. These later values can be found in the works of Davies [128] and Lin and Marszall [129]. More recently, an improvement of this equation has been proposed by Guo *et al.* [130] using effective chain length instead of the actual chain length. The so obtained group contribution was used to compute HLB values for 224 nonionic surfactants. Comparisons with experimental values have shown Average Absolute Error (AAE) less than 1.5 which is much better than the AAE of 7.3 obtained with the Davies' equation.

Table 3 gathers statistical coefficients for some QSPR models developed to predict the HLB of surfactants. Chen *et al.* [131] have proposed two high performance QSPR models for anionic surfactants: one for alkylsulfonates and alkylsulfates compounds and the other for polyoxyethylene, acetate, proprionate and fluorinated anionic surfactants. Regarding the prediction of the HLB for nonionic surfactants, Gad and Khairou [133] have developed multilinear regressions on the basis of various molecular descriptors such as the dipole moment, the octanol/water partition coefficient, the molar volume, etc. No work was found regarding the HLB prediction for cationic surfactants using QSPR methods.

CONCLUSIONS AND PERSPECTIVES

In previous sections, we have presented a review of recent progress on the use of multiscale molecular modeling tools for the prediction of surfactants' properties. The feasibility of the use of methods such as MD, MC, DPD and QSPR for the prediction of the CMC, IFT and/or HLB has been investigated.

Nearly none of the reported MD and MC studies have been carried out with the purpose of an industrial application and most of them have been done under academic considerations. From a methodological point of view, most of molecular simulations which use an atomistic description of the systems have been performed through the MD technique which is efficient for the sampling of dense phases. MC simulations are more appropriate to the study of the aggregation process, the kind and the shape of micelles. Most of the reported MC simulations have been performed using a lattice approach, with the drawback of the parameterization including a physical meaning. One can remark that works have proposed to overcome this problem using simplified electrostatic interactions but the impact on later studies measured through the number of citations, still remains negligible.

DPD simulations as a coarse-graining method allow simulations of large and complex systems. In particular, it is shown that the method can give insights on spatial organization of surfactants, interesting mechanistic informations for films evolution or trends on surface tensions regarding structure of the adsorbed tensioactive molecules at an interface. Even if ways of parameterizations of DPD simulations are already proposed, a lot of work has yet to be done to find robust and general methods to calculate input parameters for valuable simulations of realistic systems. This challenge is one of the key conditions for a successful complete multiscale modeling DPD aims to speed up the surfactant screening process [136].

Statistical methods gathered under the acronym QSPR appear as interesting tools to quickly estimate surfactants' properties. A series of models for properties such as the CMC, IFT and the HLB have already been developed and have shown good predictive ability when applied to an external set of amphiphiles, *i.e.* molecules outside of the training set. Although the CMC has been extensively studied through QSPR approaches, prediction could be improved using larger databases and techniques leading to non-linear models such as ANN or SVM. Few works have been devoted to the IFT prediction for surfactants using QSPR methods and this represents an interesting challenge for the forthcoming years. Regarding the HLB prediction, this work has put more emphasis on the need of larger databases and on the lack of QSPR models for cationic surfactants. It is also important to draw reader's attention to the fact that only properties of pure surfactants have been considered in the literature while industrial products are mostly mixtures of surfactants and the development of QSPR models for mixtures belongs to challenges of forthcoming years [137]. Finally, one can mention QSPR models for the prediction of the toxicity of surfactants which were developed on the basis of surfactant's properties such as the

HLB, the hydrophobicity (log P), the CMC or the number of carbon atoms in the hydrophobic fragment [138, 139].

ACKNOWLEDGMENTS

REFERENCES

1 Mohan K., Gupta R., Mohanty K.K. (2011) Wettability altering secondary oil recovery in carbonate rocks, *Energy Fuels* **25**, 3966-3973.

2 Brown L. (2010) Microbial Enhanced Oil Recovery (MEOR), *Curr. Opinion Microbiol.* **50**, 316-320.

3 Sun S., Zhang Z., Luo Y., Zhong W., Xiao M., Yi W., Yu L., Fu P. (2011) Exopolysaccharide production by a genetically engineered *Enterobacter cloacae* strain for microbial enhanced oil recovery, *Bioresour. Technol.* **102**, 6153-6158.

4 www.fossil.energy.gov

5 Samanta A., Ojha K., Mandal A. (2011) Interactions between acidic crude oil and alkali and their effects on enhanced oil recovery, *Energy Fuels* **25**, 1642-1649.

6 Gubbins K.E., Moore J.D. (2010) Molecular modeling of matter: Impact and prospects in engineering, *Ind. Eng. Chem. Res.* **49**, 3026-3046.

7 Theodorou D.N. (2010) Progress and outlook in Monte Carlo simulations, *Ind. Eng. Chem. Res.* **49**, 3047-3058.

8 Maginn E.J., Elliott J.R. (2010) Historical perspective and current outlook for molecular dynamics as a chemical engineering tool, *Ind. Eng. Chem. Res.* **49**, 3059-3078.

9 Moeendarbary E., Ng T.Y., Zangeneh M. (2009) Dissipative particle dynamics: Introduction, methodology and complex fluid applications - A review, *Int. J. Appl. Mech.* **1**, 737-763.

10 Moeendarbary E., Ng T.Y., Zangeneh M. (2010) Dissipative particle dynamics in soft matter and polymeric applications - A review, *Int. J. Appl. Mech.* **2**, 161-190.

11 Katritzky A.R., Kuanar M., Slavov S., Hall C.D., Karelson M., Kahn I., Dobchev D.A. (2010) Quantitative correlation of physical and chemical properties with chemical structure: utility for prediction, *Chem. Rev.* **110**, 5714-5789.

12 Torres L., Moctezuma A., Avendaño J.R., Muñoz A., Gracida J. (2011) Comparison of bio- and synthetic surfactants for EOR, *J. Petrol. Sci. Eng.* **76**, 6-11.

13 Viduna D., Milchev A., Binder K. (1998) Monte Carlo simulation of micelle formation in block copolymer solutions, *Macromol. Theory Simul.* **7**, 649-658.

14 Floriano M.A., Caponetti E., Panagiotopoulos A.Z. (1999) Micellization in model surfactant systems, *Langmuir* **15**, 3143-3151.

15 da Rocha S.R.P., Johnston K.P., Rossky P.J. (2002) Surfactant-modified CO_2-water interface: A molecular view, *J. Phys. Chem. B* **106**, 13250-13261.

16 Stone M.T., Rossky P.J., Johnston K.P. (2003) Water interface, *J. Phys. Chem. B* **107**, 10185-10192.

17 Chanda J., Bandyopadhyay S. (2005) Molecular dynamics study of a surfactant monolayer adsorbed at the air/water interface, *J. Chem. Theory Comput.* **1**, 963-971.

18 Larson R.G., Scriven L.E., Davis H.T. (1985) Monte-Carlo simulation of model amphiphilic oil-water systems, *J. Chem. Phys.* **83**, 2411-2420.

19 Wijmans C.M., Linse P. (1995) Modeling of nonionic micelles, *Langmuir* **11**, 3748-3756.

20 Kusaka I., Oxtoby D.W. (2001) A Monte Carlo simulation of nucleation in amphiphilic solution, *J. Chem. Phys.* **115**, 4883-4889.

21 Milchev A., Bhattacharya A., Binder K. (2001) Formation of block copolymer micelles in solution: A Monte Carlo study of chain length dependence, *Macromolecules* **34**, 1881-1893.

22 Lísal M., Hall C., Gubbins K.E., Panagiotopoulos A. (2002) Micellar behavior in supercritical solvent-surfactant systems from lattice Monte Carlo simulations, *Fluid Phase Equilib.* **194-197**, 233-247.

23 Rodriguez-guadarrama L., Ramanathan S., Mohanty K., Vasquez V. (2004) Molecular modeling of binary mixtures of amphiphiles in a lattice solution, *Fluid Phase Equilib.* **226**, 27-36.

24 Israelachvili J.N., Mitchell D.J., Ninham B.W. (1976) Theory of self-assembly of hydrocarbon amphiphiles into micelles and bilayers, *J. Chem. Soc. Faraday Trans. 2* **72**, 1525-1568.

25 Sammalkorpi M., Sanders S., Panagiotopoulos A.Z., Karttunen M., Haataja M. (2011) Simulations of micellization of sodium hexyl sulfate, *J. Phys. Chem. B* **115**, 1403-1410.

26 Talsania S., Wang Y., Rajagopalan R., Mohanty K. (1997) Monte Carlo simulations for micellar encapsulation, *J. Colloid Interface Sci.* **190**, 92-103.

27 Talsania S.K., Rodríguez-Guadarrama L.A., Mohanty K.K., Rajagopalan R. (1998) Phase behavior and solubilization in surfactant/solute/solvent systems by Monte Carlo simulations, *Langmuir* **14**, 2684-2692.

28 Mackie A.D., Panagiotopoulos A.Z., Szleifer I. (1997) Aggregation behavior of a lattice model for amphiphiles, *Langmuir* **13**, 5022-5031.

29 Pool R., Bolhuis P.G. (2005) Accurate free energies of micelle formation, *J. Phys. Chem. B* **109**, 6650-6657.

30 Cavallo A., Müller M., Binder K. (2006) Formation of micelles in homopolymer-copolymer mixtures: A quantitative comparison between simulations of long chains and self-consistent field calculations, *Macromolecules* **39**, 9539-9550.

31 Gharibi H., Behjatmanesh-Ardakani R., Hashemianzadeh M., Mousavi-Khoshdel M. (2006) Complexation between a macromolecule and an amphiphile by Monte Carlo technique, *J. Phys. Chem. B* **110**, 13547-13553.

32 Hashemianzadeh S.M., Gharibi H., Mousavi-Khoshdel S.M., Sohrabi B., Safarpoor M.A. (2008) Lattice Monte Carlo simulation of dilute ionic surfactants, *J. Mol. Liq.* **138**, 147-154.

33 Jorge M. (2008) Molecular dynamics simulation of self-assembly of *n*-decyltrimethylammonium bromide micelles, *Langmuir* **24**, 5714-5725.

34 Stephenson B.C., Beers K., Blankschtein D. (2006) Complementary use of simulations and molecular-thermodynamic theory to model micellization, *Langmuir* **22**, 1500-1513.

35 Stephenson B.C., Goldsipe A., Beers K.J., Blankschtein D. (2007) Model for the micellization of nonionic surfactants in aqueous solution, *J. Phys. Chem. B* **111**, 1045-1062.

36 Stephenson B.C., Goldsipe A., Blankschtein D. (2008) Molecular dynamics simulation and thermodynamic modeling of the self-assembly of the triterpenoids asiatic acid and madecassic acid in aqueous solution, *J. Phys. Chem. B* **112**, 2357-2371.

37 Samanta S.K., Bhattacharya S., Maiti P.K. (2009) Coarse-grained molecular dynamics simulation of the aggregation properties of multiheaded cationic surfactants in water, *J. Phys. Chem. B* **113**, 13545-13550.

38 Maiti P.K., Lansac Y., Glaser M.A., Clark N.A., Rouault Y. (2002) Self-assembly in surfactant oligomers: A coarse-grained description through molecular dynamics simulations, *Langmuir* **18**, 1908-1918.

39 Marrink S.J., De Vries A.H., Mark A.E. (2004) Coarse grained model for semiquantitative lipid simulations, *J. Phys. Chem. B* **108**, 750-760.

40 Burov S.V., Vanin A.A., Brodskaya E.N. (2009) Principal role of the stepwise aggregation mechanism in ionic surfactant solutions near the critical micelle concentration. Molecular dynamics study, *J. Phys. Chem. B* **113**, 10715-10720.

41 Sanders S.A., Panagiotopoulos A.Z. (2010) Micellization behavior of coarse grained surfactant models, *J. Chem. Phys.* **132**, 114902.

42 Kirkwood J.G., Buff F.P. (1949) The statistical mechanical theory of surface tension, *J. Chem. Phys.* **17**, 338-343.

43 Blokhuis E.M., Bedeaux D., Holcomb C.D., Zollweg J.A. (1995) Tail corrections to the surface-tension of a Lennard-Jones liquid-vapor interface, *Mol. Phys.* **85**, 665-669.

44 Irving J.H., Kirkwood J.G. (1950) The statistical mechanical theory of transport processes. IV. The equations of hydrodynamics, *J. Chem. Phys.* **18**, 817-829.

45 Guo M., Lu B.C.-Y. (1997) Long range corrections to thermodynamic properties of inhomogeneous systems with planar interfaces, *J. Chem. Phys.* **106**, 3688-3695.

46 Janeček J., Krienke H., Schmeer G. (2006) Interfacial properties of cyclic hydrocarbons: A Monte Carlo study, *J. Phys. Chem. B* **110**, 6916-6923.

47 MacDowell L.G., Blas F.J. (2009) Surface tension of fully flexible Lennard-Jones chains: Role of long-range corrections, *J. Chem. Phys.* **131**, 074705.

48 MacDowell L.G., Bryk P. (2007) Direct calculation of interfacial tensions from computer simulation: Results for freely jointed tangent hard sphere chains, *Phys. Rev. E* **75**, 061609.

49 Gloor G.J., Jackson G., Blas F.J., de Miguel E. (2005) Test-area simulation method for the direct determination of the interfacial tension of systems with continuous or discontinuous potentials, *J. Chem. Phys.* **123**, 134703.

50 Jang S.S., Lin S.-T., Maiti P.K., Blanco M., Goddard W.A., Shuler P., Tang Y. (2004) Molecular dynamics study of a surfactant-mediated decane-water interface: Effect of molecular architecture of alkyl benzene sulfonate, *J. Phys. Chem. B* **108**, 12130-12140.

51 Ma H., Luo M., Dai L.L. (2008) Influences of surfactant and nanoparticleassembly on effective interfacial tensions, *Phys. Chem. Chem. Phys.* **10**, 2207-2213.

52 Stephenson B.C., Beers K.J. (2006) Determination of the interfacial characteristics of a series of bolaamphiphilic poly(fluorooxetane) surfactants through molecular dynamics simulation, *J. Phys. Chem. B* **110**, 19393-19405.

53 Urbina-Villalba G., Landrove R.M., Guaregua J.A. (1997) Molecular dynamics simulation of the interfacial behavior of a heptane/water system in the presence of nonylphenol entropy and interaction energies as a function of temperature and surfactant concentration, *Langmuir* **13**, 1644-1652.

54 Behjatmanesh-Ardakani R., Nikfetrat M. (2007) Study of Winsor I to Winsor II transitions in a lattice model, *J. Phys. Chem. B* **111**, 7169-7175.

55 Hoogerbrugge P.J., Koelman J.M.V.A. (1992) Simulating microscopic hydrodynamic phenomena with dissipative particle dynamics, *Europhys. Lett.* **19**, 155-160.

56 Groot R.D., Warren P.B. (1997) Dissipative particle dynamics: Bridging the gap between atomistic and mesoscopic simulation, *J. Chem. Phys.* **107**, 4423-4435.

57 Rekvig L., Frenkel D. (2007) Molecular simulations of droplet coalescence in oil/water/surfactant systems, *J. Chem. Phys.* **127**, 134701.

58 Pool R., Bolhuis P.G. (2006) Can purely repulsive soft potentials predict micelle formation correctly?, *Phys. Chem. Chem. Phys.* **8**, 941-948.

59 Li Z.L., Dormidontova E.E. (2010) Kinetics of diblock copolymer micellization by dissipative particle dynamics, *Macromolecules* **43**, 3521-3531.

60 Dzwinel W., Yuen D.A. (2000) Matching macroscopic properties of binary fluids to the interactions of dissipative particle dynamics, *Int. J. Mod. Phys. C* **11**, 1-25.

61 Ghoufi A., Malfreyt P. (2011) Local pressure components and surface tension of spherical interfaces. Thermodynamic *versus* mechanical definitions. I. A mesoscale modeling of droplets, *J. Chem. Phys.* **135**, 104105.

62 Rekvig L., Kranenburg M., Hafskjold B., Smit B. (2003) Effect of surfactant structure on interfacial properties, *Europhys. Lett.* **63**, 902-907.

63 Rekvig L., Kranenburg M., Vreede J., Hafskjold B., Smit B. (2003) Investigation of surfactant efficiency using dissipative particle dynamics, *Langmuir* **19**, 8195-8205.

64 Maiti A., McGrother S. (2004) Bead-bead interaction parameters in dissipative particle dynamics: Relation to bead-size, solubility parameter and surface tension, *J. Chem. Phys.* **120**, 1594-1601.

65 Ginzburg V.V., Chang K., Jog P.K., Argenton A.B., Rakesh L. (2011) Modeling the interfacial tension in oil-water-nonionic surfactant mixtures using dissipative particle dynamics and self-consistent field theory, *J. Phys. Chem. B* **115**, 4654-4661.

66 Li Y.M., Guo Y.Y., Bao M.T., Gao X.L. (2011) Investigation of interfacial and structural properties of CTAB at the oil/water interface using dissipative particle dynamics simulations, *J. Colloid Interface Sci.* **361**, 573-580.

67 Li Y.M., Xu G.Y., Chen Y.J., Luan Y., Yuan S.L. (2006) Computer simulations of surfactants and surfactant/polymer assemblies, *Comput. Mater. Sci.* **36**, 386-396.

68 Jury S., Bladon P., Cates M., Krishna S., Hagen M., Ruddock N., Warren P. (1999) Simulation of amphiphilic mesophases using dissipative particle dynamics, *Phys. Chem. Chem. Phys.* **1**, 2051-2056.

69 Ryjkina E., Kuhn H., Rehage H., Muller F., Peggau J. (2002) Molecular dynamics computer simulations of phase behavior of non-ionic surfactants, *Ang. Chem. Int. Ed.* **41**, 983-986.

70 Yang C.J., Chen X., Qiu H.Y., Zhuang W.C., Chai Y.C., Hao J.C. (2006) Dissipative particle dynamics simulation of phase behavior of aerosol OT/water system, *J. Phys. Chem. B* **110**, 21735-21740.

71 Illya G., Lipowsky R., Shillcock J.C. (2006) Two-component membrane material properties and domain formation from dissipative particle dynamics, *J. Chem. Phys.* **125**, 114710.

72 Shillcock J.C., Lipowsky R. (2006) The computational route from bilayer membranes to vesicle fusion, *J. Phys. Condens. Matter* **18**, S1191-S1219.

73 Zhong C.L., Liu D.H. (2007) Understanding multicompartment micelles using dissipative particle dynamics simulation, *Macromol. Theory Simul.* **16**, 141-157.

74 Schulz S.G., Kuhn H., Schmid G., Mund C., Venzmer J. (2002) Phase behavior of amphiphilic polymers: A dissipative particles dynamics study, *Colloid Polym. Sci.* **283**, 284-290.

75 Rekvig L., Hafskjold B., Smit B. (2004) Molecular simulations of surface forces and film rupture in oil/water/surfactant systems, *Langmuir* **20**, 11583-11593.

76 Groot R.D. (2000) Mesoscopic simulation of polymer-surfactant aggregation, *Langmuir* **16**, 7493-7502.

77 Groot R.D., Rabone K.L. (2001) Mesoscopic simulation of cell membrane damage, morphology change and rupture by nonionic surfactants, *Biophys. J.* **81**, 725-736.

78 Chen Z.X., Cheng X.L., Cui H.S., Cheng P., Wang H.Y. (2007) Dissipative particle dynamics simulation of the phase behavior and microstructure of CTAB/octane/1-butanol/water microemulsion, *Colloids Surf. A Physicochem. Eng. Aspects* **301**, 437-443.

79 Groot R.D. (2003) Electrostatic interactions in dissipative particle dynamics-simulation of polyelectrolytes and anionic surfactants, *J. Chem. Phys.* **118**, 11265.

80 Gonzalez-Melchor M., Mayoral E., Velazquez M.E., Alejandre J. (2006) Electrostatic interactions in dissipative particle dynamics using the Ewald sums, *J. Chem. Phys.* **125**, 224107.

81 Ibergay C., Malfreyt P., Tildesley D.J. (2009) Electrostatic Interactions in Dissipative Particle Dynamics: Toward a Mesoscale Modeling of the Polyelectrolyte Brushes, *J. Chem. Theory Comput.* **5**, 3245-3259.

82 Ibergay C., Malfreyt P., Tildesley D.J. (2010) Mesoscale Modeling of Polyelectrolyte Brushes with Salt, *J. Phys. Chem. B* **114**, 7274-7285.

83 Tropsha A. (2010) Best practices for QSAR model development, validation and exploitation, *Mol. Inf.* **29**, 476-488.

84 Chirico N., gramatica P. (2011) Real external predictivity of QSAR models: How to evaluate it? Comparison of different validation criteria and proposal of using the concordance correlation coefficient, *J. Chem. Inf. Model.* **51**, 2320-2335.

85 Hu J., Zhang X., Wang Z. (2010) A review on progress in QSPR studies for surfactants, *Int. J. Mol. Sci.* **11**, 1020-1047.

86 Rosen M.J. (1976) The relationship of structure to properties in surfactants. IV. Effectiveness in surface or interfacial tension reduction, *J. Colloid Interface Sci.* **56**, 320-327.

87 Becher P. (1984) Hydrophile-lipophile balance: history and recent developments, *J. Dispers. Sci. Technol.* **5**, 81-96.

88 Ravey J.C., Gherbi A., Stébé M.J. (1988) Comparative study of fluorinated and hydrogenated nonionic surfactants. I. Surface activity properties and critical concentrations, *Prog. Colloid Polym. Sci.* **76**, 234-241.

89 Huibers P.D.T., Lobanov V.S., Katritzky A.R., Shah D.O., Karelson M. (1996) Prediction of critical micelle concentration using a quantitative structure-property relationship approach. 1. Nonionic surfactants, *Langmuir* **12**, 1462-1470.

90 Huibers P.D.T., Lobanov V.S., Katritzky A.R., Shah D.O., Karelson M. (1997) Prediction of critical micelle concentration using a Quantitative structure-property relationship approach. 2. Anionic Surfactants, *J. Colloid Interface Sci.* **187**, 113-120.

91 Anoune N., Nouiri M., Berrah Y., Gauvrit J.-Y., Lanteri P. (2002) Critical micelle concentrations of different classes of surfactants: A quantitative structure property relationship study, *J. Surfactant. Deterg.* **5**, 45-53.

92 Wang Z. (2002) A quantitative structure-property relationship study for the prediction of critical micelle concentration of nonionic surfactants, *Colloids Surf. A Physicochem. Eng. Aspects* **197**, 37-45.

93 Yuan S., Cai Z., Xu G., Jiang Y. (2002) Quantitative structure-property relationships of surfactants: Prediction of the critical micelle concentration of nonionic surfactants, *Colloid Polym. Sci.* **280**, 630-636.

94 Saunders R.A., Platts J.A. (2004) Correlation and prediction of critical micelle concentration using polar surface area and LFER methods, *J. Phys. Org. Chem.* **17**, 431-438.

95 Gad E.A.M. (2007) QSPR for nonionic surfactants, *J. Dispers. Sci. Technol.* **28**, 231-237.

96 Katritzky A.R. (2008) QSPR study of critical micelle concentrations of nonionic surfactants, *Ind. Eng. Chem. Res.* **47**, 9687-9695.

97 Mozrzymas A., Rózycka-Roszak B. (2010) Prediction of critical micelle concentration of nonionic surfactants by a quantitative structure-property relationship, *Comb. Chem. High Throughput Screening* **13**, 39-44.

98 Roy K., Kabir H. (2012) QSPR with extended topochemical atom (ETA) indices: Modeling of critical micelle concentration of non-ionic surfactants, *Chem. Eng. Sci.* **73**, 86-98.

99 Jalali-Heravi M., Konouz E. (2003) Multiple Linear Regression Modeling of the Critical Micelle Concentration of Alkyltrimethylammonium and Alkylpyridinium Salts, *J. Surfactant. Deterg.* **6**, 25-30.

100 Katritzky A.R., Pacureanu L., Slavov S., Dobchev D., Shah D., Karelson M. (2009) QSPR study of the first and second critical micelle concentrations of cationic surfactants, *Comput. Chem. Eng.* **33**, 321-332.

101 Mozrzymas A., Rózycka-Roszak B. (2011) Prediction of critical micelle concentration of cationic surfactants using connectivity indices, *J. Math. Chem.* **49**, 276-289.

102 Jalali-Heravi M., Konouz E. (2000) Prediction of critical micelle concentration of some anionic surfactants using multiple regression techniques: A quantitative structure-activity relationship study, *J. Surfactant. Deterg.* **3**, 47-52.

103 Yuan S., Cai Z., Xu G., Jiang Y. (2002) Quantitative structure-property rlationships of surfactants: critical micelle concentration of anionic surfactants, *J. Dispers. Sci. Technol.* **23**, 465-472.

104 Roberts D.W. (2002) Application of octanol/water partition coefficients in surfactant science: A quantitative structure-property relationship for micellization of anionic surfactants, *Langmuir* **18**, 345-352.

105 Li X., Zhang G., Dong J., Zhou X., Yan X., Luo M. (2004) Estimation of critical micelle concentration of anionic surfactants with QSPR approach, *J. Mol. Struct. Theochem.* **710**, 119-126.

106 Katritzky A.R., Pacureanu L., Dobchev D., Karelson M. (2007) QSPR study of critical micelle concentration of anionic surfactants using computational molecular descriptors, *J. Chem. Inf. Model.* **47**, 782-793.

107 Stanton D.T. (2008) On the importance of topological descriptors in understanding structure-property relationships, *J. Comput. Aided Mol. Design* **22**, 441-460.

108 Absalan G., Hemmateenejad B., Soleimani M., Akhond M., Miri R. (2004) Quantitative structure-micellization relationship study of gemini surfactants using genetic-PLS and genetic-MLR, *QSAR Comb. Sci.* **23**, 416-425.

109 Kardanpour Z., Hemmateenejad B., Khayamian T. (2005) Wavelet neural network-based QSPR for prediction of critical micelle concentration of gemini surfactants, *Anal. Chim. Acta* **531**, 285-291.

110 Guo C.W., Zhou P., Shao J., Yang X.C., Shang Z.C. (2011) Integrating statistical and experimental protocols to model and design novel Gemini surfactants with promising critical micelle concentration and low environmental risk, *Chemosphere* **84**, 1608-1616.

111 Bhhatarai B., Gramatica P. (2011) Prediction of aqueous solubility, vapor pressure and critical micelle concentration for aquatic partitioning of perfluorinated chemicals, *Environ. Sci. Technol.* **45**, 8120-8128.

112 Wang Z.-W., Li G.-Z., Mu J.-H., Zhang X.-Y., Lou J. (2002) Quantitative structure-property relationship on prediction of surface tension of nonionic surfactants, *Chinese Chem. Lett.* **13**, 363-366.

113 Wang Z.-W., Huang D.-Y., Li G.-Z., Zhang X.Y., Liao L.-L. (2003) Effectiveness of surface tension reduction by anionic surfactants - quantitative structure-property relationships, *J. Dispers. Sci. Technol.* **24**, 653-658.

114 Wang Z.-W., Feng J.-L., Wang H.-J., Cui Z.-G., Li G.-Z. (2005) Effectiveness of surface tension reduction by nonionic surfactants with quantitative structure-property relationship approach, *J. Dispers. Sci. Technol.* **26**, 441-447.

115 Fini M.F., Riahi S., Bahramian A. (2012) Experimental and QSPR studies on the effect of ionic surfactants on *n*-Decane-Water interfaciale tension, *J. Surfactant. Deterg.* **15**, 477-484.

116 Needham D.E., Wei I.-Chien, Seybold P.G. (1988) Molecular modeling of the physical properties of alkanes, *J. Am. Chem. Soc.* **110**, 4186-4194.

117 Stanton D.T., Jurs P.C. (1990) Development and use of charged partial surface area structural descriptors in computer-assisted quantitative structure-property relationship studies, *Anal. Chem.* **62**, 2323-2329.

118 Stanton D.T., Jurs P.C. (1992) Computer-assisted study of the relationship between molecular structure and surface tension of organic compounds, *J. Chem. Inf. Model.* **32**, 109-115.

119 Liu S., Cai S., Cao C., Li Z. (2000) Molecular Electronegative Distance Vector (MEDV) related to 15 properties of alkanes, *J. Chem. Inf. Comput. Sci.* **40**, 1337-1348.

120 Knotts T.A., Wilding W.V., Oscarson J.L., Rowley R.L. (2001) Use of the DIPPR database for development of QSPR correlations: Surface tension, *J. Chem. Eng. Data* **46**, 1007-1012.

121 Kauffman G.W., Jurs P.C. (2001) Prediction of surface tension, viscosity and thermal conductivity for common organic solvents using quantitative structure-property relationships, *J. Chem. Inf. Comput. Sci.* **41**, 408-418.

122 Shamsipur M., Ghavami R., Hemmateenejad B., Sharghi H. (2004) Highly correlating distance-connectivity-based topological indices. 2: Prediction of 15 properties of a large set of alkanes using a stepwise factor selection-based PCR analysis, *QSAR Comb. Sci.* **23**, 734-753.

123 Delgado E.J., Diaz G.A. (2006) A molecular structure based model for predicting surface tension of organic compounds, *SAR QSAR Environ. Res.* **17**, 483-496.

124 Wang J., Du H., Liu H., Yao X., Hu Z., Fan B. (2007) Prediction of surface tension for common compounds based on novel methods using heuristic method and support vector machine, *Talanta* **73**, 147-156.

125 Khajeh F., Modarress H. (2011) Quantitative structure-property relationship for surface tension of some common alcohols, *J. Chemom.* **25**, 333-339.

126 Gharagheizi F., Eslamimanesh A., Mohammadi A.H., Richon D. (2011) Use of artificial neural network-group contribution method to determine surface tension of pure compounds, *J. Chem. Eng. Data* **56**, 2587-2601.

127 Gharagheizi F., Eslamimanesh A., Tirandazi B., Mohammadi A.H., Richon D. (2011) Handling a very large dataset for determination of surface tension of chemical compounds using quantitative structure-property relationship strategy, *Chem. Eng. Sci.* **66**, 4991-5023.

128 Davies J.T. (1957) A quantitative kinetic theory of emulsion type. I. Physical chemistry of the emulsifying agent, *Proc. 2nd Int. Congr. Surface Activity*, Butterworths, London, **1**, 426-438.

129 Lin I.J., Marszall L. (1976) CMC, HLB, and effective chain length of surface-active anionic and cationc substances containing oxyethylene groups, *J. Colloid Interface Sci.* **57**, 85-93.

130 Guo X., Rong Z., Ying X. (2006) Calculation of the hydrophile-lipophile balance for polyethoxylated surfactants by group contribution method, *J. Colloid Int. Sci.* **298**, 441-450.

131 Chen M.-L., Wang Z.-W., Zhang G.-X., Wang W.-D. (2007) Prediction on hydrophile-lipophile balance values of anionic surfactants with QSPR method, *Acta Chim. Sinica* **65**, 1265-1272.

132 Chen M.-L., Wang Z.-W., Duan H.-J. (2009) QSPR for HLB of nonionic surfactants using two simple descriptors, *J. Dispers. Sci. Technol.* **30**, 1481-1485.

133 Gad E.A.M., Khairou K.S. (2008) QSPR for HLB of nonionic surfactants based on polyoxyethylene group, *J. Dispers. Sci. Technol.* **29**, 940-947.

134 Liu S.L., Tong J.B., Li Y.F. (2009) QSPR study of the hydrophile-lipophile balance values of anionic surfactant, *Guangdong Chem.* **36**, 64-65.

135 Luan F., Liu H., Gao Y., Li Q., Zhang X., Guo Y. (2009) Prediction of the hydrophile-lipophile balance values of anionic surfactants using a quantitative structure-property relationship, *J. Colloid Int. Sci.* **336**, 773-779.

136 Buijse M., Tandon K., Jain S., Handgraaf W., Fraaije J.G.E.M. (2012) Surfactants optimization for EOR using advanced chemical computational methods, *SPE International*, SPE paper 154212.

137 Muratov E.N., Varlamova E.V., Artemenko A.G., Polishchuk P.G., Kuz'min V.E. (2012) Existing and developing approaches for QSAR analysis of mixtures, *Mol. Inf.* **31**, 202-221.

138 Lindgren A., Sjostrom M., Wold S. (1996) QSAR modelling of the toxicity of some technical non-ionic surfactants towards fairy shrimps, *Quant. Struct.-Property Relationship* **15**, 208-218.

139 Jurado E., Fernandez-Serrano M., Nunez-Olea J., Luzon G., Lechuga M. (2009) Acute toxicity and relationship between metabolites and ecotoxicity during the biodegradation process of non-ionic surfactants: fatty-alcohol ethoxylates, nonylphenol polyethoxylate and alkylpolyglucosides, *Water Sci. Technol.* **59**, 2351-2358.