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CONFORMATIONS OF HYDROPHOBIC CHAINS AT LIQUID/GAS INTERFACE AND THEIR IMPLICATIONS ON SURFACTANT ADSORPTION[#]

We present a simple model of single chain, non-ionic surfactant adsorption at gas/liquid interface. Our model takes explicitly into account the effect of conformations the surfactant hydrocarbon chains can assume at the interface. We applied our model for the description of a dependence of surface tension on solution concentration of homologous series of n-alkanols. Aliphatic alcohols with the chain length from four to ten carbon atoms were studied. We found that our model correctly describes experimental data and predicts a distribution of chain conformation at the interface for all n-alkanols studied. We detected small but distinct even-odd effect in the distribution of conformations.

Key words: surfactants, adsorption, hydrocarbon chains, conformationsk

INTRODUCTION

Modification of interfacial properties of various interfaces is a key issue for mineral processing. For instance in the process of flotation a decrease of surface tension and increase of surface elasticity of air/water interface favors bubble production of the desired size and enhance foamability. Due to their amphiphatic molecular structure surfactants, when present at low concentration in solution, have the property of adsorbing onto surfaces or interfaces of the system and altering to a significant degree their interfacial properties. In order to optimize the choice of surfactant for a specific application, the fundamental information concerning its equilibrium and dynamic adsorption properties have to be known. This properties are obviously controlled by the structure of surfactant molecule itself. Water soluble surfactants typically consist of the hydrophilic ionic, non-ionic or zwitterionic head-

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group and hydrophobic part, which for simple surfactants is a single hydrocarbon chain. For the same head-group, length of the chain, i.e. the position of a given surfactant in a homologous series, decides on its surface activity. The unrestricted hydrocarbon chain is quite flexible and therefore, can assume many conformation when exposed into gas phase at aqueous solution/air interface. When adsorption progresses and the interface becomes crowded with surfactant, less area is accessible for a single chain. Therefore, some conformations with the highest area are strongly restricted. This decrease of the conformational freedom should lead to decrease of the free energy of adsorption, therefore, should be reflected in the adsorption equilibrium isotherm and also in the adsorption kinetics.

In our paper we propose a simple model to describe the effect of conformations of hydrophobic chains at interface on adsorption. We verify the implications of our model on the experimental data concerning the dependence of surface tension on concentration of the homologous series of the simplest surface active species – n-alkanols.

THEORETICAL BACKGROUND

Consider adsorption equilibrium between surfactant in bulk and interface. Formally we can write the criterion of the equilibrium in terms of chemical potentials in bulk μ_b and surface phase μ_s:

$$\mu_b = \mu_0^b + kT \ln(\gamma c)$$

$$\mu_s = \mu_0^s + kT \ln(\gamma_s \Gamma) \tag{1}$$

where: μ_0^b and μ_0^s is the standard chemical potential of the surfactant in bulk and at interface respectively, c is surfactant concentration in solution, Γ is its surface concentration, γ and γ_s are respective surfactant activity coefficients in bulk and at interface. For dilute solutions $\gamma \approx 1$. In the equilibrium the chemical potentials are equal and that leads to a general adsorption isotherm in a form:

$$\gamma_s \Gamma = \gamma c \exp\left(-\frac{\Delta\mu_0}{kT}\right) \tag{2}$$

where: $\Delta\mu_0$ - the standard free energy of adsorption (per one molecule) i.e. energy of transfer of molecule from the bulk of the solution to empty interface. Surfactant activity coefficient at the interface can be expressed in terms of free energy of interactions with solvent and other surfactant molecules:

$$\gamma_s = exp\left(-\frac{\Delta\mu_{int}}{kT}\right) \tag{3}$$

We assume that this free energy consists of several additive terms (Ben Shaul et al., 1985, Warszyński and Lunkenheimer, 1999):

$$\Delta\mu_{int}(\Gamma) = \Delta\mu_{hg-hg} + \Delta\mu_{hg-ch} + \Delta\mu_{ch-ch} + \Delta\mu_{conf} \tag{3}$$

Here, $\Delta\mu_{hg-hg}$ - is the head-group interaction free energy which originates mainly from the excluded volume interactions between head-groups, $\Delta\mu_{hg-ch}$ - is the free energy of other head-group\head-group or head-group\chain interactions, $\Delta\mu_{ch-ch}$ - is free energy of the van der Waals cohesive interaction between hydrocarbon chains, $\Delta\mu_{conf}$ - is conformational free energy of surfactant tails involving all possible chain conformations resulting from the intrachain C-C bonds rotations and rotations of entire surfactant molecule at the interface.

For example, if we assume that the head-group interaction free energy can be expressed as (Nagarayan and Ruckenstein, 1977):

$$\Delta\mu_{hg-hg} = -kT\ln\left(1 - \frac{A_{hg}}{A}\right) = -kT\ln(1-\theta) \tag{4}$$

where: A_{hg} is the cross-sectional area of the headgroup, $A = \dfrac{1}{N_a\Gamma}$ is the area per molecule adsorbed, $\theta = \dfrac{A_{hg}}{A} = \dfrac{\Gamma}{\Gamma_\infty}$ is the surface coverage and Γ_∞ is the limiting surface concentration corresponding to the closely packed monolayer. Additionally, we express second and third component in the Eq. (4) in terms of mean field approximation (Rowlinson and Widom, 1989):

$$\Delta\mu_{hg-ch} + \Delta\mu_{ch-ch} = -2H\Gamma \tag{5}$$

where H is a mean field parameter, and if we neglect the conformational contribution, we arrive at Frumkin isotherm:

$$\frac{c}{a} = \frac{\theta}{1-\theta}\exp\left(-\frac{2H_s}{kT}\theta\right) \tag{6}$$

which is commonly used for the description of surfactants' adsorption. Here, a is the surface activity parameter or the bulk-surface distribution coefficient and $H_s = \dfrac{H}{A_{hg}}$ is the Frumkin interaction parameter assuming positive values for attractive interactions favoring adsorption.

The hydrocarbon chain is quite flexible due to low energy difference (~ 1.2 kT) between trans (t) and gauche (g^+, g^-) conformation of four consecutive carbon atoms in the chain (dihedral angles) (Flory, 1971). Therefore, for long chains it exists a considerable amount of conformations which are energetically accessible. Figure 1. presents an example of such conformations for n-hexanol. The number of conformations of surfactant at the interface is restricted because a surfactant molecule is anchored to it by the head-group and penetration of solution sublayer by surfactant tail is limited.
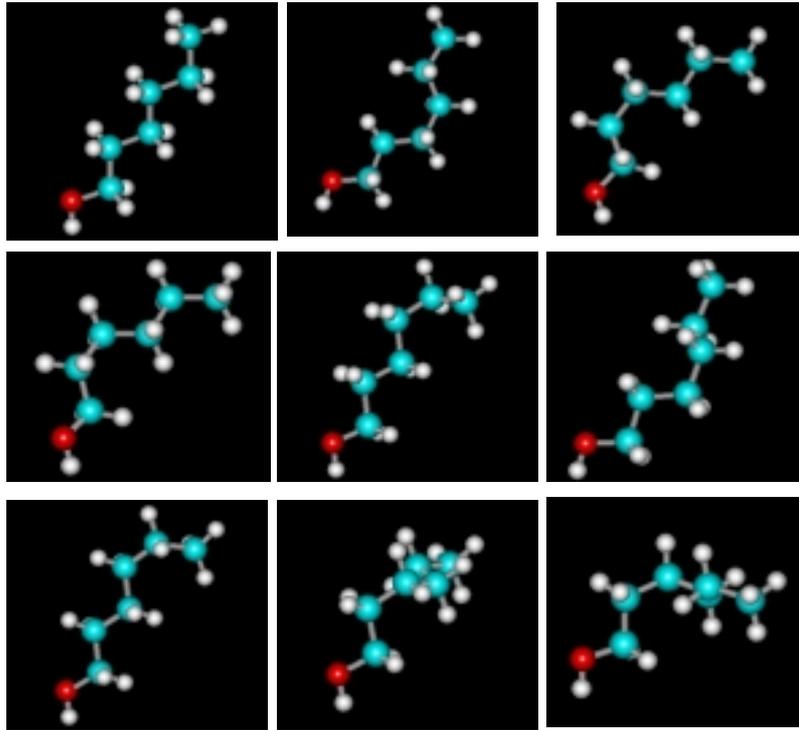

Fig. 1. Examples of conformations of n-hexanol molecule

Conformational free energy of surfactant has to be evaluated from (Ben Shaul et al., 1985):

$$\Delta \mu_{conf} = - k\, T \ln z_{conf} \tag{7}$$

where: z_{conf} is the effective partition function (configurational sum) of a single surfactant tail at the interface :

$$z_{conf} = \sum_{\{a_i\}} \exp\left(-\frac{\varepsilon(a_i)}{k\,T} \right) \tag{8}$$

where: $\{a_i\}$ is a set of all possible tail conformations, i.e. all possible sequences of trans and gauche conformations of dihedral angles in a hydrocarbon chain and all possible orientations of the entire chain at the interface, $\varepsilon(a_i)$ the energy of the chain in conformation a_i consisting of bonds bending energies, torsional energies of C-C bonds' rotations, the van der Waals and hard core interactions between distant (separated by more than four C-C bonds) CH_2 and/or CH_3 groups of the same chain. As it was demonstrated by Vold (Vold 1984) with the procedure of exhaustive enumeration one can determine the cumulative distribution of surfactant conformations in terms of effective area occupied by a given conformation at interface, A_c. Taking into account the interaction of the surfactant tail with water subphase (which was not done by Vold), this distribution can be approximated with gamma function:

$$f_{conf}\left(A_c(a_i)\right) \approx \left(A_c(a_i) - A_{CH_2}\right)^{\alpha} \exp\left(-\frac{A_c(a_i) - A_{CH_2}}{\beta}\right) \qquad (9)$$

where two parameters α and β describe shape of the distribution and A_{CH_2} is the limiting effective cross-sectional area of the chain in all trans-conformation, 0.20 nm^2 (see the top left picture in Fig.1.). Knowing the distribution of the chain conformations, one can determine the dependence of the single chain conformational partition function on surfactant surface concentration using a very simple model. At the low coverage surfactant chains does not contact with each other and all conformations possible to attain at the interface are available. Thus, replacing the sum over conformations by integration over the distribution of effective areas of a chain in Eq.(9) we obtain:

$$z_{conf}(\infty) = \int_{A_{CH_2}}^{\infty} f'_{conf}(A_c)\, d A_c \qquad (10)$$

When the interface is partially covered with surfactant at the surface concentration equal to Γ we assume that all conformations with the effective area less than A per two surfactant chains are equally possible, whereas conformations with the effective area higher than A are prohibited by the excluded volume interactions with the neighboring chains. Thus,

$$z_{conf}(A) = \int_{A_{CH_2}}^{A} f'_{conf}(A_c)\, d A_c \qquad (11)$$

where: $f'_{conf}\left(A_c(a_i)\right) = \left(\frac{A_c(a_i) - A_{CH_2}}{2}\right)^{\alpha} \exp\left(-\frac{A_c(a_i) - A_{CH_2}}{2\beta}\right)$

The difference of the conformational free energy per one molecule adsorbed at partially covered and empty interface is then given by:

$$\Delta\mu_{conf} = -\,k\,T\,\ln\frac{z_{conf}(A)}{z_{conf}(\infty)} \qquad (12)$$

Combining Eqs. (2) – (6) with Eq. (13) we obtain modified Frumkin isotherm which explicitly takes into account the surfactant chain conformations:

$$\frac{c}{a} = \frac{\theta}{(1-\theta)}\exp(-\frac{2H_s}{kT}\theta)\exp\left(\frac{\Delta\mu_{conf}}{k\,T}\right) \qquad (13)$$

More details of the model are given elsewhere (Warszyński and Lunkenheimer 1999).

To compare predictions of the model with experimental data for the dependence of surface tension, σ, of surfactant solution on its concentration, c_b, we integrate the Gibbs adsorption equation:

$$\sigma(c_b) = \sigma_0 - k\,T\int_0^{c_b}\Gamma\,d\ln c = \sigma_0 - k\,T\,\Gamma_\infty\int_0^{\theta(c_b)}\frac{\theta}{c}\frac{dc}{d\theta}d\theta \qquad (14)$$

where σ_0 is the surface tension of water, using adsorption isotherms given by Eq.(14) and assuming that surface concentration is approximately equal to surface excess concentration in the sense of Gibbs.

RESULTS AND DISCUSSION

Figure 2. presents a dependence of the surface tension on the concentration of aqueous solution of n-alkanols with the carbon number ranging from four (n-butanol) to ten (n-decanol). Surface tension was determined using Lauda tensiometer with du Noüy ring. All necessary corrections for measurements in soluble systems (Lunkenheimer and Wantke, 1981) were applied. The experimental error of a single measurement was 0.2 mN/m.

Aliphatic alcohols: n-butanol (Merck), n-pentanol, n-hexanol, n-heptanol, n-octanol and n-nonanol (Sigma) of analytical purity grade were used as received. Results for n-decanol presented in Fig. 2. were obtained using the same technique (Warszyński et al. 2002). The n-alkanols have been chosen because the size of hydroxyl headgroup is smaller than cross-section of the hydrocarbon chain. Therefore, the effect of conformational changes should be considerable, unscreened by the excluded volume headgroup-headgroup interactions. In Fig. 2. symbols represent experimental data while lines show fits to the theoretical model. Best fit parameters are presented in Table 1. The quality of the fit was evaluated according to the condition that the mean square fitting

error:

$$s = \sqrt{\sum_{i=1}^{m} \frac{(\sigma_{ex}(c_i) - \sigma_{ev}(c_i))^2}{f_g}} \quad (15)$$

where $\sigma_{ex}(c_i)$ is the measured surface tension at a given concentration, $\sigma_{ev}(c_i)$ is the surface tension calculated according to the model adsorption isotherm, m is the number of experimental points, $f_g = n - m - 1$ is the number of the degree of freedom and n is the number of fitted parameters.

Table I. Values of the best fit parameters for homologous series of n-alkanols. $\Gamma_\infty = 8.5 \cdot 10^{-10}$ mol/cm^2, common for all n-alkanols was selected to reflect the limiting area per one molecule attained for insoluble aliphatic alcohols in Langmuir monolayer at maximal compression (Lunkenheimer and Miller, 1986)

| n-alkanol	a [mol/dm^3]	H_s [kJ/mol]	<A> [nm^2]	σ_A [nm^2]	s [mN/m]
n–butanol (C4)	$8.2 \cdot 10^{-2} \pm 2 \cdot 10^{-3}$	0.6±0.2	0.27±0.01	0.052±0.005	0.11
n-pentanol (C5)	$3.5 \cdot 10^{-2} \pm 2 \cdot 10^{-3}$	2.2±0.3	0.30±0.02	0.07±0.007	0.26
n-hexanol (C6))	$1.1 \cdot 10^{-2} \pm 5 \cdot 10^{-4}$	3.3±0.2	0.31±0.01	0.075±0.007	0.21
n-heptanol (C7)	$3.5 \cdot 10^{-3} \pm 1 \cdot 10^{-4}$	4.5±0.2	0.33±0.02	0.085±0.008	0.29
n-octanol (C8)	$1.6 \cdot 10^{-3} \pm 2 \cdot 10^{-5}$	6.1±0.4	0.34±0.02	0.1±0.008	0.32
n-nonanol (C9)	$5.5 \cdot 10^{-4} \pm 6 \cdot 10^{-6}$	7.4±0.2	0.37±0.01	0.117±0.005	0.19
n-decanol (C10)	$2.4 \cdot 10^{-4} \pm 5 \cdot 10^{-6}$	8.2±0.2	0.38±0.02	0.118±0.008	0.29
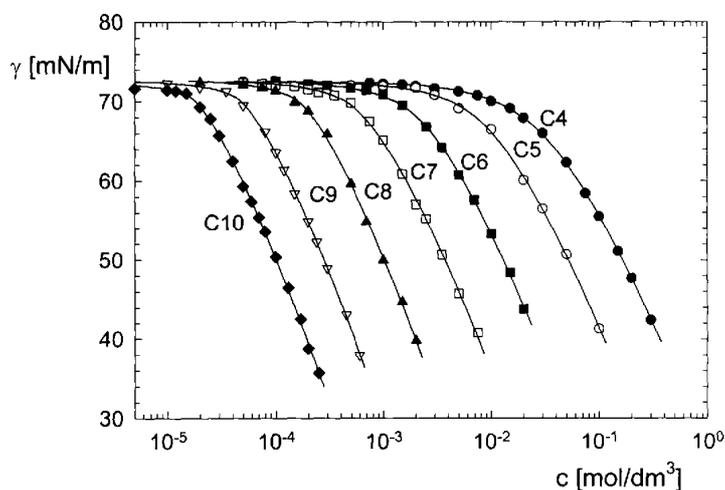
Fig. 2. Dependence of surface tension on concentration of solutions of homologous series of n-alkanols

Surface activity of n-alkanols ranges from $5 \cdot 10^{-5}$ for n-decanol to 10^{-1} mol/dm^3 for the shortest n-butanol. As the results presented in Fig. 2. suggest the description of the experimental data in terms of the model presented above for all n-alkanols in the

homologous series is very good. Basing on the best fit values of parameters of the model we determined the distribution of cross-sectional area taken by hydrocarbon chain conformations at interface for all members of homologous series. Results are presented in Figure 3.
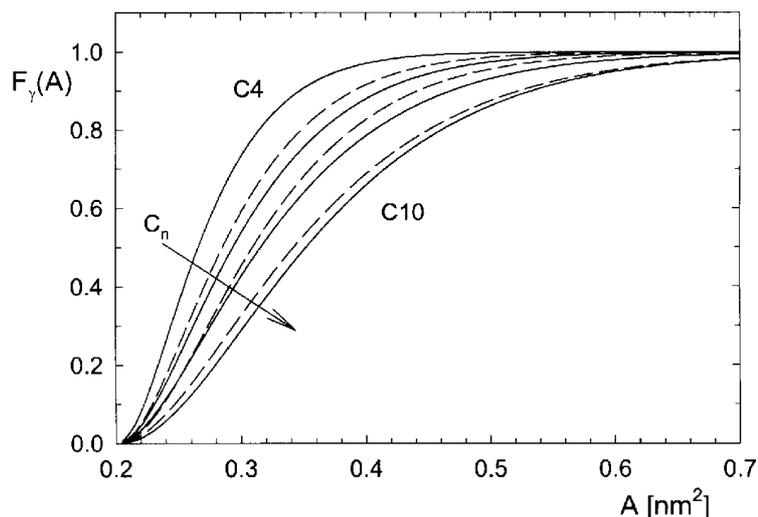

Fig. 3. Distribution of the effective cross-sectional area of hydrocarbon chain conformations for n-alkanols obtained from the best fit of Eq. (14) to the experimental data shown in Fig. 2. Distributions for chains containing odd number of carbons are shown as dashed lines.

As it is illustrated in Fig. 3. the effective size of n-butanol conformations at air/solution interface ranges from 0.20 nm^2 for the chain in trans conformation to ca. 0.35 nm^2 which correspond to tilted gauche conformation. On the other hand, the range of effective size of n-decanol conformations is much broader. The chain containing n carbon atoms can assume 3^{n-3} conformations of dihedral angles. Some of these conformation are energetically unfavorable (e.g. containing of $g^{+}g^{-}$ sequence (Flory, 1971)), some are restricted due to the presence of the interface but there is still a considerable number of them which can be assumed by the chain. Moreover, longer chain poses more rotational freedom at the interface and both this factors are reflected in broad distribution of effective sizes. The results shown in Fig. 3. suggest noticeable even-odd effect in the distribution of conformations. Hydrocarbon chains consisting of odd number of carbon atoms tend to assume at the interface on the average more expanded conformations than chains with even number of carbons. It is also illustrated in Figure 4. where the dependence of the mean effective cross-sectional area of the hydrocarbon chain for the homologous series of n-alkanols is plotted as a function of the number of carbon atoms in the chain.
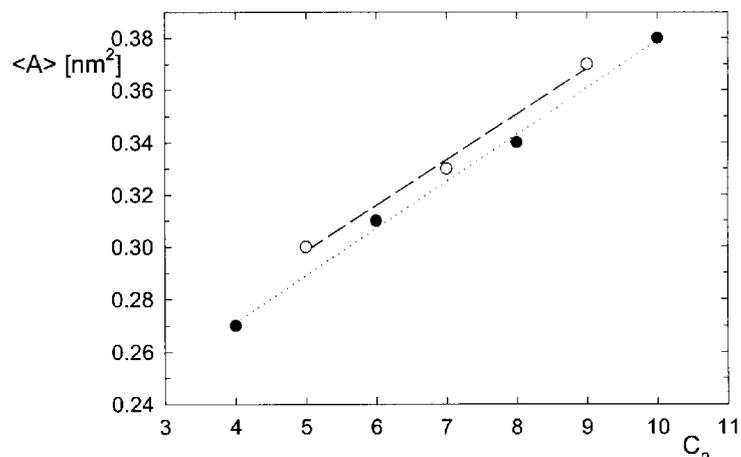
Fig. 4. Dependence of the average effective cross-sectional area of the hydrocarbon chain at interface on the number of carbon atoms

As it can be seen the average effective cross-sectional area of the hydrocarbon chain for even and odd members of the homologous series of n-alkanols can be arranged along two distinct lines. Similar effect was observed in liquid crystals, where chains with even number of carbon atoms were able to pack more effectively (Marcelja, 1974).

CONCLUSIONS

We presented a simple model of single chain, non-ionic surfactant adsorption which explicitly takes into account the distribution of the chain conformations. Every conformation has an effective cross-sectional area at the interface. When adsorption progresses and the interface becomes crowded with surfactant, conformations which occupy large space are restricted. That leads to a decrease of the chain conformational freedom and consequently to a decrease of free energy of adsorption. We checked the implications of our model by applying it for the description of dependence of surface tension on concentration of solutions of homologous series of n-alkanols. It occurred that our model adequately describes experimental data and predicts the variation of effective cross-sectional area determined by a distribution of conformations of chains for all studied n-alkanols. We detected small but distinct even-odd effect in the distribution of conformations.

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SYMBOL LIST

$\{a_i\}$ - a set of all possible tail conformations a_i,

c, c_b – surfactant concentration in solution,

f_g - number of the degree of freedom,

m - the number of experimental points,

n - number of fitted parameters of the isotherm.

z_{conf} - is the effective partition function of a single surfactant tail at the interface,

A - the area per molecule adsorbed,

A_{hg} is the cross-sectional area of the headgroup,

A_{CH_2} - the limiting effective cross-sectional area of the chain in all trans- conformation,

H – mean field interaction parameter,

H_s – Frumkin interaction parameter,

α - parameter of Gamma function,

β - parameter of Gamma function,

γ - surfactant activity coefficients in bulk,

γ_s - surfactant activity coefficients at interface,

$\varepsilon(a_i)$ the energy of the chain in conformation a_i,

$\mu_0{}^b$ - the standard chemical potential of the surfactant in bulk,

$\mu_0{}^s$ - the standard chemical potential of the surfactant at interface,

σ - surface tension of a solution,

σ_0 – surface tension of water,

$\sigma_{ex}(c_i)$ - the measured surface tension at a given concentration,

$\sigma_{ev}(c_i)$ - the surface tension calculated according to the model adsorption isotherm,

θ - surfactant surface coverage,

$\Delta\mu_0$ - the standard free energy of adsorption (per one molecule),

$\Delta\mu_{hg\text{-}hg}$ - the head-group excluded volume interaction free energy,

$\Delta\mu_{hg\text{-}ch}$ - the free energy of other head-group\head-group or head-group\chain interactions, $\Delta\mu_{ch\text{-}ch}$ - is free energy of the van der Waals cohesive interaction between hydrocarbon chains,

$\Delta\mu_{conf}$ - is conformational free energy of surfactant tails,

Γ - surfactant surface concentration,

Γ_{∞} - the limiting surfactant surface concentration,

Warszyński P., Jachimska B., *Wpływ konformacji hydrofobowych łańcuchów na powierzchni roztwór/gaz na adsorpcję prostych substancji powierzchniowoczynnych,* Fizykochemiczne Problemy Mineralurgii, 36, (2002) 38-49 (w jęz. ang.)

Zaprezentowano prosty model adsorpcji na swobodnej powierzchni roztworu dla niejonowych surfaktantów o pojedynczym łańcuchu węglowodorowym. Model ten bezpośrednio uwzględnia efekt swobody konformacyjnej łańcuchów na powierzchni. Został oparty na założeniu, że izolowany łańcuch na powierzchni może przyjmować wszystkie energetycznie dozwolone konformacje związane obrotem wokół wiązań C-C w obrębie łańcucha, jak i jego rotacji jako całości. Wraz ze wzrostem adsorpcji konformacje o dużym efektywnym polu powierzchni są wzbronione co prowadzi do spadku entropii a w konsekwencji do spadku swobodnej energii adsorpcji. Model został zastosowany do opisu zależności napięcia powierzchniowego wodnych roztworów szeregu homologicznego alkoholi alifatycznych o długościach łańcucha od czterech do dziesięciu atomów węgla. Stwierdzono, że model dobrze opisuje wyniki doświadczalne i pozwala przewidzieć rozkłady efektywnego pola zajmowanego przez łańcuchy węglowodorowe w różnych konformacjach na powierzchni. Rozkłady te silnie zależą od długości łańcucha - liczby atomów węgla - jak również w pewnym stopniu od tego czy w łańcuchu znajduje się ich nieparzysta bądź parzysta ilość.