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Effect of molecular structure of amphiphiles on the surface pressure and electric surface potential isotherms at the air/solution interface

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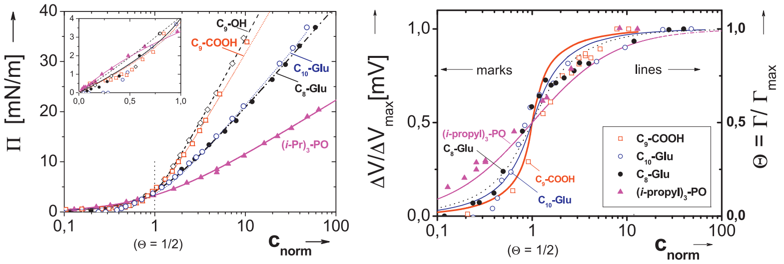
HIGHLIGHTS

- Adsorption properties of soluble surfactants of different molecular structure are compared.
- Surface pressure and the electric surface potential vs. concentration isotherms are analyzed.
- Frumkin model is fitted to the experimental surface pressure vs. concentration isotherms.
- Shape of the normalized isotherms with respect to half surface coverage concentration is compared.
- The electric surface potential isotherms imply change of effective dipole moment with coverage.

GRAPHICAL ABSTRACT

Surface pressure (π) and electric surface potential (ΔV) isotherms of soluble surfactants, when presented in concentration scale normalized with respect to half surface coverage concentration, $c_{norm} = c/c_{\Theta/2}$ (which may conveniently be derived from Frumkin model), enable examination of differences in shape caused by amphiphiles' different structure. The coverage $\Theta \le 50\%$ makes at the most 25% of the total π and 50% of the total ΔV change.



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ABSTRACT

Surface pressure vs. concentration, $\pi - c$, and electric surface potential, $\Delta V - c$, isotherms at free surface of aqueous solutions of selected amphiphiles were analyzed with respect to (i) size of the head group, (ii) length of paraffinic chain and (iii) presence of branched chain of the comparable number of C atoms. The Frumkin isotherm was fitted to the measured $\pi - c$ dependencies and the results were examined as a function of concentration normalized with respect to the concentration of the half surface coverage, $c_n = c/c_{\Theta/2}$, derived from the best fit Frumkin parameters. The largest variation in shape of the π vs. c_n isotherms was found between amphiphiles possessing different head groups substituted with comparable paraffin chains (C_8–C_9). Their isotherms in the high coverage region ($\Theta > 50\%$) exhibited notably diverse slopes, $d\pi/d \log c_n$, indicating significantly different surface excess of the amphiphiles. The minimum "cross-sectional areas" calculated from the fitted parameter Γ_∞, as $A_{\min} = 1/N\Gamma_\infty$, are slightly higher than the hard-core cross-sectional area of the most bulky part of free molecule which indicates a residual hydration of the saturated monolayers. The identical value of $A_{\min} = 27.7$ Å^2/molec. found for the *n*-alkanols series (C_4–C_9) is significantly greater than minimum cross-section area of hard core of the fully extended chain, ca. 21.3 Å^2. On the other hand, the $A_{\min}$ area found for glucopyranosides (ca. 45 Å^2/molec.) correlates with smaller cross-section of the "ellipsoidal" head group (ca. 40 Å^2), suggesting its nearly perpendicular inclination to the interface plane in the saturated monolayer. The normalized electric surface potential isotherms, $\Delta V/\Delta V_{\max}$ vs. c_n, deviate from the Frumkin $\Theta - c_n$ dependencies, in particular, in the higher coverage range, $\Theta > 50\%$, which implies change of the effective dipole moment, $\mu_\perp$, and/or the local permittivity, ε_s, with Θ.

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1. Introduction

Understanding of the interfacial behavior of surfactants at air–liquid interfaces is crucial for many aspects of colloid science and practical applications. The interfacial properties of surfactant solutions play a major role in thin film and foam stability, micellization, emulsification, emulsion stability, flotation, etc. The most important property of surfactants is their ability to lower the surface tension of solution at relatively low concentrations. That is described by the Gibbs adsorption equation, which for solution of a single, non-ionic surfactant can be written in the form:

$$d\sigma = -RT\Gamma d\mu \tag{1}$$

where σ is the surface tension of the solution, Γ is the Gibbs surface excess concentration and μ is the chemical potential of the surfactant. For dilute solutions, Γ is approximately equal to surface concentration and the Gibbs equation assumes the form:

$$d\sigma = -RT\Gamma d\ln c \tag{2}$$

where c is the bulk concentration of surfactant.

Second fundamental relationship describing surfactant system is an adsorption isotherm, which connects surface and bulk concentration of surfactant molecules, $\Gamma = \Gamma(c)$. Many models of surfactant adsorption, and consequently, many adsorption isotherms have been proposed, so far. Generally, they may be grouped together as describing localized and non-localized adsorption (in sense of the adsorption energy barrier which may be much higher or lower than the thermal energy, respectively) or describing the interfacial phase in terms of theory of regular solutions or 2D phases. Good review of classical isotherms most frequently used for describing surfactant adsorption at the air/water interface can be found in [1–4]. The classical models silently assume that single molecule possesses only one conformation at the interface which is equivalent to the assumption that surface pressure isotherm is determined by the surface excess, only. Models of the greater complexity assume a dependence of surface pressure on ratio of at least two adsorbate states – distinguishable from orientation [5], partial molar area [6,7]) or a 2D phase's domains (mostly liquid condensed) spread within a less denser 2D phase (liquid expanded or gas) [8–10]. The lately proposed model by Warszyński and Lunkenhiner [11] regards the whole spectrum of conformation/orientation states which depend on the surface concentration. On the other hand, the recently developed aggregation model [12–14] considers a spectrum of adsorbate clusters which involves some assumptions concerning the aggregates' distribution which results in a greater number of adjustable parameters (4–5) as compared to the classical models (2–3). The aggregation model was found providing a better fit to dynamic surface tension data ($\pi - t$) of n-nonanol [13] and n-decanol [2,8] as compared to the classical models. However, it was shown [2,8,13], that, the same set of dynamic surface tension data ($\pi - t$) and the equilibrium isotherms ($\pi - c$) [4] may satisfactory be fitted with different models, such as, the generalized Frumkin model (involving a dependence of the interactions parameter on Γ) or 2D phase transition model. It implies that a good conformity of some of the models to the experimental results could be reached without their physicochemical adequateness. Although, the above mentioned advanced models of nonionic surfactant adsorption are now available, the classical Frumkin isotherm – formulated in the twenthieths in the twentieth century [15a,b,16], is very convenient to be used as the first approximation. This view is supported by a vast number of reports that adsorption of non-ionic surfactants of a moderate chain length, $C_n \leq 9$, at the air/water interface, is satisfactory describable with the classical Frumkin model [1]. However, it remains still an open question to what extent the best-fit Frumkin parameters reflect their defined physical interpretation and they can be related to the molecular properties of surfactant. Therefore, question of correlation of isotherm' parameters with surfactant molecular structure is of practical importance when we would like to predict interfacial behavior of molecule of known structure.

The aim of the paper was to examine influence of structure of selected amphiphiles on shape of the surface pressure (π) vs. concentration (c) isotherms at free surfaces of aqueous solutions and to show to what degree the parameters of the simple and commonly used Frumkin isotherm [15a,b,16] can reflect molecular structure. The equilibrium $\pi - c$ and $\Delta V - c$ isotherms obtained by us for selected simple surfactants are analyzed in respect to the influence of (i) size of the head group (n-decanoic acid, n-decanol, n-octyl- and n-decyl-β-D-glucopyranosides), (ii) length of paraffinic chain (n-alkanols: C_4, C_6, C_8, C_9), or (iii) presence of branched chain of comparable number of carbon atoms (C_9) such as in the paraffinic chains of the other molecules discussed (tri-isopropylphosphine oxide). The surface excess (Γ) vs. concentration (c) dependences derived from the best-fit Frumkin parameters are used for evaluating the electric surface potential (ΔV) vs. concentration (c) isotherms, measured concurrently with the surface pressure.

2. Theoretical background

The Frumkin isotherm [15a,b,16] is written as follows:

$$Bc = \Gamma_\infty \frac{\Theta}{1-\Theta} \exp\left(-2\frac{H^s}{RT}\Theta\right) \tag{3}$$

with $\Theta = \Gamma/\Gamma_\infty$, was fitted to the experimental $\pi = f(c)$ dependencies and the characteristic parameters: Γ_∞ – the maximum surface excess, B – the parameter related to the adsorption equilibrium constant, and H^s – the standard enthalpy of intermolecular interactions at the interface, were found for the surface active species studied. For $H^s = 0$, Frumkin isotherm transforms into a Langmuir-type isotherm describing the "ideal" (in the sense of ideal entropy of surface mixing) behavior. The experimental and theoretical results were compared as a function of concentration normalized with respect to the concentration of half surface coverage, $c_n = c/c_{\Theta/2}$, which, according to Frumkin isotherm, is expressed as follows:

$$c_{\Theta/2} = \frac{\Gamma_\infty}{B}\exp(-H^s/RT) = a_n \exp(-H^s/RT) \tag{4}$$

where $a_n = \Gamma_\infty/B$. The normalized concentration scale brings the ranges of surface activity of surfactants – separated by several or more orders of magnitude when expressed in molar concentration, into a similar range around the value of $c_n = 1$ (corresponding to the surface coverage of $\Theta = 50\%$). In this scale, the isotherms' shapes of surfactants with different surface activities can be conveniently compared.

For lack of a more detailed theory, the electric surface potential, ΔV, of adsorption monolayers (the adsorption potential shift) at the air/solution [17–31] or a liquid/liquid [31], as well as mercury/solution [15,16,18,19] interfaces are commonly evaluated in terms of the interfacial double layer capacitor which for nonionic adsorbates at no electrolyte presence is formed by dipoles of all molecules at the interface (of the solute and the solvent). The Helmholtz equation – commonly used for describing ΔV may be written as follows:

$$\Delta V = \frac{N_A \Gamma_\infty}{\varepsilon_0}\theta\frac{\mu_l}{\varepsilon_l} \tag{5}$$

where N_A is the Avogardro number, ε_s and ε_0 are permittivity of the interface plane (the local value) and of vacuum, respectively, the $\Theta = \Gamma/\Gamma_\infty$ is the surface coverage found by fitting the experimental $\pi - c$ data with an adsorption model, $\mu_\perp$ – named the effective dipole moment is the perpendicular component of dipole moment vector of adsorbate molecule, averaged out the monolayer. Since, the value of ε_s is not known and numerous approximate