Ideal (Langmuir-type) surface and electric properties of tert- isopropylphosphine oxide at the air/water interface

Abstract The surface pressure (π) and electric surface potential (ΔV) of tert-isopropylphosphine oxide (i-Pr₃PO) were measured at the air/water interface. Solutions matching the criterion of “surface-chemical purity” were investigated. Measurable effects on π and ΔV are revealed at 1 × 10⁻⁴ mol/dm³ i-Pr₃PO and extend throughout three concentration decades. The initial rise of the surface potential with the concentration is several times steeper compared to that of the surface tension. The dependence of the surface tension on the concentration of i-Pr₃PO is well described by a Langmuir-type isotherm. Furthermore, the relation between ΔV and the surface concentration (Γ₅) calculated using the Langmuir isotherm is linear. Such consistency with the Langmuir-type adsorption throughout the entire surface activity range is an uncommon feature among soluble surfactants. The ideal surface properties of i-Pr₃PO are mainly due to the ellipsoidal hard-sphere-like structure of the molecule delimited by the isopropyl chain, which determines the closest packing density of the adsorbate. This is justified by the minimum cross-sectional area of about 80 Å²/molecule adsorbed, which corresponds to a sphere delimited by the length of the fully extended isopropyl chain (5 Å). The other reason for the ideal surface behavior is the compatibility of the dimensions of an i-Pr₃PO molecule with an average water cluster (of 13 H₂O). The slope (ε₀ dΔV/dΓ₅) determines the effective dipole moment (per molecule) μₜ/ε₀ = 1.2 ± 0.1 D. This relatively high value of μₜ/ε₀ is a result of the dipole moments of the highly polar ≡P = O head group and of six –CH₃ terminal groups. Owing to the radial distribution of the terminal groups around the head group, the effective dipole moment is practically independent of the molecule’s conformation at the surface.

Key words Alkylphosphine oxide surfactant · Surface pressure · Electric surface potential · Effective dipole moment

Introduction

The common purpose of the theoretical description of adsorption of surface-active substances is to find reliable values of the standard functions of adsorption: the Gibbs free energy, ΔG⁰, the entropy, ΔS⁰ and the Helmholtz free energy, ΔH⁰, for comparing surface properties of different surfactants. The most convenient way to do so, is to describe the experimental results in terms of one of the basic equations of surface state, reviewed in Refs. [1, 2]; however, for the majority of soluble surfactants, none of these theoretical surface pressure isotherms can be fitted to experimental results without notable deviation. In such a case, an isotherm
fit may be improved by applying different approaches, also reviewed in Refs. [1, 2].

The possible methods are as follows:

1. A series expansion of an adsorption isotherm (by introducing virial coefficients).
2. Fitting the basic isotherm with some parameters which are a function of the surfactant concentration in the bulk and at the interface.
3. Superimposing two (or more) adsorption isotherms.

The latter approach was explored in earlier work of one of the authors [3, 4], who superposed two of these basic equations of surface state – Henry–Langmuir and/or Henry–Frumkin isotherms. Recently, another approach was proposed by one of the authors [5], who introduced the conformational term to the Frumkin isotherm (as to the universal equation for liquid interfaces). This term is attributed to the changes in the conformation of the adsorbate with increasing adsorption density. An attempt has also been made to correlate the changes in the conformations with the experimentally observed variations of the electric surface potential [6, 7].

The surfactants containing the phosphoryl head group (≡P=O), like alkylphosphine oxides, were the subject of recent investigations by one of the authors [8, 9]. They are of particular interest with respect to the influence of the branched hydrophobic chain (characterizing a “bulky” molecule) on the surface and electric properties of a soluble monolayer at the air/water interface. As shown previously [8, 9], the surfactants of the phosphine oxide type show a medium surface activity, extending throughout a relatively wide region, usually of about three concentration decades.

In this article we report the results of surface tension and electric surface potential measurements that we obtained for tert-isopropylphosphine oxide (t-iPr3PO). Its peculiarity, as compared to other “bulky” surfactants, is the hydrophobic part composed of three short isopropyl chains; the substituents filling three valences of the phosphoryl head group, with the phosphorous atom in a tetrahedral arrangement. As illustrated in Fig. 1, the i-Pr3PO structure corresponds to a hard sphere like an ellipsoid flattened on the side of the head group (the pivot of the molecule). This structure should not undergo any conformational changes at the interface. The length of the isopropyl chain, which is about 5 Å in the fully extended state, determines the distance between the centers of the i-Pr3PO molecules at the highest packing density. As this limiting distance almost exceeds the range of van der Waals interactions (around 10 Å [10]), one can expect that van der Waals interactions between the adsorbate molecules are negligible. Moreover, the radius of an i-Pr3PO molecule is comparable to that of a water cluster (composed of 13 water molecules, on average [11]); therefore, the adsorbate may easily replace the cluster from the air/water interface. Such an exchange does not induce a noticeable structural change of water, so it is characterized by a very low standard entropy of adsorption. We note here that the i-Pr3PO molecule is in a state of “hydrophobic hydration” [11], which means a “clathrate hydrate”, i.e., a state of embedding in a water cluster under dynamic equilibrium.

The molecular properties of i-Pr3PO suggest it should be a suitable surfactant to exhibit ideal surface behavior within the entire range of the surface activity region; however, the ideal properties have to be verified not only by the good suitability of a Langmuir-type isotherm to the experimental surface tension results (which is not the ultimate criterion), but also by the analysis of the adsorption data as a function of the temperature; The latter has to fulfill the corresponding dependence

Fig. 1 Structural model of tert-isopropylphosphine oxide (t-iPr3PO)