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Adsorption of poly(ethylene oxide) at the air/water interface: A dynamic and static surface tension study

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Abstract

The adsorption of polyethylene oxide (PEO) homologues in a wide range of molecular weight (from $M_{\text{PEO}} = 200$ to 10^6) at the air/aqueous solution interface was investigated by dynamic and static surface tension measurements. An approximate estimate for the lower limit of PEO concentration was given at which reliable equilibrium surface tension can be determined from static surface tension measurements. It was shown that the observed jump in the earlier published $\sigma - \lg(c_{\text{PEO}})$ curves is attributable to the nonequilibrium surface tension values at low PEO concentrations. The adsorption behavior of short chain PEO molecules ($M_{\text{PEO}} \leqslant 1000$) is similar to that of the ordinary surfactants. The estimated standard free energy of PEO adsorption, ΔG^0, increases linearly with the PEO molecular weight until $M_{\text{PEO}} = 1000$. In this molecular weight range, ΔG^0 was found to be approximately the fifth of the hydrophobic driving force related to the adsorption of a surfactant with the same number of methylene groups. In the case of the longer chain PEOs the driving force of adsorption is so high that the adsorption isotherm is near saturation in the experimentally available polymer concentration range. Above a critical molecular weight the PEO adsorption reveals universal features, e.g., the surface tension and the surface density of segments do not depend on the polymer molecular weight.

Keywords: Polymer adsorption; Fluid/fluid interface; Equilibration criteria; Macromolecule; Surface tension; Adsorption driving force

1. Introduction

The adsorption properties of polymers have been investigated for a long time because of their importance in the fundamental surface science as well as their relevance in the efficiency of a variety of industrial formulations. However, the quantitative description of the surface layer at the air/water interface is still subjected to considerable experimental and theoretical difficulties. One of the most intensively used methods has been the surface tension technique and the Gibbs equation has been applied to determine the adsorbed amount of nonionic macromolecules at the free aqueous surface. However, there are several fundamental problems in connection with this widely used practice. Fleer et al. have pointed out first [1] that the polymers are multicomponent systems and without the detailed knowledge of the chain length and surface activity distribution of the different components the basic expression of the surface thermodynamics cannot be practically used.

Another important drawback is the lack of the detailed knowledge of the concentration dependence of the polymer activity coefficients [2]. In the semidilute and concentrated aqueous solutions of poly(ethylene oxide) [2–5] and poly(vinylpyrrolidone) [6] a peculiar adsorption behavior, e.g., an additional significant surface tension reduction, was found which might be attributable to the significant decrease in the solvency of the polymers and the complex concentration dependence of their activity at the high concentration range.

On the other hand, even in dilute polymer solutions with fairly narrow distribution of the components anomalies have been reported for a variety of systems. Namely, a sudden upturn in the surface tension has been observed at low polymer concentrations which was followed with a nearly linear, shallow part of the $\sigma - \lg(c_{\text{pol}})$ curves [2–9]. A possible interpretation for this phenomenon was suggested by Linse et al. [10] who explained the convex part in the $\sigma - \lg(c_{\text{pol}})$ curves in terms of a surface depletion effect in the dilute concentration regime. Very

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recently, An et al. have elegantly proved for the adsorption of poly(vinyl methyl ether), via the sophisticated application of the neutron reflection method, that the surface tension anomaly is attributable to the nonequilibrated surface layer at the low concentration regime [9]. Therefore, it can be concluded that a reliable control of the adsorption equilibrium is of paramount importance in the determination of adsorption isotherms from surface tension data.

In this work the focus is on the surface properties of polyethyleneoxide (PEO), which is a well-known water soluble polymer with a very complex solution and phase behavior [11,12]. The adsorption of PEO at the air/water interface has been intensively investigated by a variety of methods like surface tension measurements [2–5,13–18], ellipsometry [3,4], surface light scattering [2,5], and neutron reflection [17,18]. In these studies equilibration problems were reported for the dilute solutions of longer chain polyethylene oxides. Qualitatively different adsorption behavior of the small and the large PEO molecules was also observed and controversial trends in the "equilibrium" adsorption characteristics as a function of macromolecular size were reported [13–16]. Couper et al. observed nearly linear $\sigma-\lg(c_{\mathrm{PEO}})$ curves for intermediate molecular weight PEOs [14]. In other works an upward jump in the $\sigma-\lg(c_{\mathrm{PEO}})$ curves was observed at the dilute PEO concentration range, followed by a nearly constant shallow part at larger concentrations [2–5,13,15,16] and several authors applied the Gibbs equation in the dilute concentration range as well [13,15]. Lu et al. also observed a convex part of the $\sigma-\lg(c_{\mathrm{PEO}})$ curves followed by an approximately linear part with small slope at large PEO concentrations [18]. However, the analysis of the neutron reflection data was found to be consistent only with the linear part of the surface tension isotherms but did not support the surface tension data observed in the dilute regime [18].

In the present study the adsorption of PEO from dilute solution on its free aqueous interface is investigated with high precision dynamic and static surface tension measurements. One of the main objectives of the present work is to provide appropriate practical criteria, by means of experimentally available parameters, which are necessary for the reliable determination of the values of the equilibrium surface tension. Furthermore, we also aim to elucidate and compare the equilibrium adsorption isotherms of the PEO samples ranging from the size of small molecules ($M_{\mathrm{PEO}} \approx 200$) to the typical molecular weight of large macromolecules ($M_{\mathrm{PEO}} \approx 10^6$). Finally, the surface tension data will be analyzed in the framework of a simple adsorption model and the chain length dependent driving force of PEO adsorption will be discussed.

2. Materials and methods

2.1. Materials

The investigated polyethylene oxides were Aldrich products. The PEO molecular weights were accepted as claimed by the manufacturer. According to the classical investigations the reaction mechanism of the PEO syntheses suggests a narrow (Poisson) distribution of the molecular weight [19]. This prediction was also proved in Ref. [20] where commercial PEO samples (which included Aldrich products as well) were investigated by size exclusion chromatography and $M_{\mathrm{w}}/M_{\mathrm{n}} < 1.04$ values were found for $M_{\mathrm{PEO}} \leqslant 35{,}000$. Altogether eleven samples with different molecular weight were used for the investigations ($M_{\mathrm{PEO}} = 200$, 400, 600, 900, 1500, 2000, 4600, 8000, 35,000, 10^5, 10^6). For the preparation of polymer solutions ion-exchanged, doubled distilled water was used.

2.2. Dynamic surface tension

Pendant drop measurements were used for monitoring the changes of the surface tension in time. A detailed description of both the applied apparatus and its operative principles has been given elsewhere [21]. The drops were formed in a closed, temperature-controlled chamber at $25.00 \pm 0.05\,^\circ\mathrm{C}$. In order to avoid the evaporation of the pendant drop, the sidewalls of the chamber were covered with wetted filter paper (the volume decrease of the drop did not exceed 1% during several hours). Prior to the surface tension measurements a series of drops was formed at the tip of the capillary, thus ensuring the creation of a clean surface. The time required for the formation of a pendant drop was approximately 1 s. After the formation of the third pendant drop, the syringe pump was stopped and the monitoring of the drop shape started ($t = 0$). A picture of the pendant drop was taken at every 5 s, and the recorded sequential digital images were used for the calculation of the surface tension values on the basis of the Laplace equation [21]. The accuracy and reproducibility of the determined surface tension values were ±0.1 mN/m. The dynamic surface tension measurements were performed for the samples of $M_{\mathrm{PEO}} = 8000$, 35,000, and 10^5.

2.3. Static surface tension

During the static measurements the surface tension was calculated from the maximum force measured by the Wilhelmy plate method using a 2.0 cm wide and 0.2 mm thick platinum plate. The measurements were performed in a cylindrical cell of 8 cm diameter at $25.00 \pm 0.05\,^\circ\mathrm{C}$. The reproducibility of the maximum force was $\pm 2 \times 10^{-6}$ N (that corresponds to ±0.05 mN/m surface tension). Prior to the measurements the solution surface was sucked off to form a fresh surface. The surface tension was accepted as an equilibrium value when it became independent from the time within the experimental error. Building on the results of the dynamic surface tension measurements the applied polymer concentration range was specifically chosen for each polymer to ensure the approximate range of equilibration time between a few minutes and 1 h. At lower PEO concentrations significantly longer equilibration times were observed and the surface tension values were found not to be reproducible.

The adsorption isotherms were calculated from the measured surface tension data by means of the Gibbs equation assuming monodisperse polymers:

$$\Gamma = -\frac{1}{RT}\left(\frac{\partial \sigma}{\partial \ln(\gamma c)}\right)_{T,p}, \tag{1}$$