Measurement of interaction forces between crossed quartz glass rods in presence of adsorbed macromolecules

Th. Götze¹), H. Sonntag¹), and Ya. Rabinovitch²)

¹) Institute of Physical Chemistry, AdW DDR, Berlin, G.D.R., and
²) Institute of Physical Chemistry, ANSSSR, Moscow, U.S.S.R.

Abstract: The interaction energy-distance curves of fractionated and unfractionated homo- and copolymers were measured. The results were compared quantitatively with the HVO theory. It was found that only a small number of segments per tail are necessary to obtain stability. The experimental energy-distance curves for low molecular weights are described sufficiently well by the HVO theory, with exponential distribution of tail sizes. For high molecular weights the exponential distribution cannot be considered as a reasonable assumption because the number of segments in the tails is very low.

Polydisperse samples of PVA with different contents of acetate groups, and similar molecular weight, indicate an increasing extension of the adsorbed polymer layer with decreasing acetate content.

Key words: Interaction force, adsorbed polymer, structure.

Introduction

An experimental method has been developed for determining interaction forces between two macroscopic surfaces covered with adsorbed macromolecules as a function of their separation. We have used the technique of crossed rods [1, 2]. The interaction forces between two rods are converted to a proportional rotational movement of a transducer which is working like an electrical galvanometer. The distance between the interacting surfaces is measured indirectly. The interaction forces between the penetrating layers become measurable at surface separations of about 130 nm (within an error of ± 5 nm) with forces of about 10^{-8} N. At distances of 20 nm the interaction forces increase steeply from about 10^{-6} N without any measurable decrease of the distance.

One of the principal ways of enhancing the stability of colloidal dispersions is to cover the particles with polymer or surfactant molecules; they produce steric repulsion in addition to electrostatic repulsion. The present knowledge about steric hindrance is still insufficient compared with the knowledge about double layer or van der Waals interaction [3, 4].

In this paper experimental results of steric repulsion of different polymer samples are compared with theoretical calculations according to Hesselink-Vrij-Overbeek (HVO) theory [5] and with the theory of adsorption of interacting polymer chains [6, 7].

Methods

The measuring device used was recently described [2]. A special cell was constructed from stainless steel; the gasket rings were made of Teflon. Quartz glass filaments were fixed outside this box and protruded through small holes into the cell. The cell was filled with polymer solution with the aid of a special pump, so that the two filaments were immersed under the liquid. The volume of the box was about 300 cm^3 and it was filled with 250 cm^3 solution. There were two stop-clocks outside the cell for the passage of liquid. The pH value of the solution was measured before and after the experiments. The temperature was measured with a glass thermistor. The filaments were prepared from quartz glass (Herasil III). Before starting the experiments the steel box was cleaned with concentrated chromic sulphuric acid at 333 K for 5 min and washed with twice-distilled water. All polymer solutions were made with twice-distilled water which was filtered through 50 nm filters in a pressure filtration apparatus. The pH of the water was 6.5 and the specific conductance 3 \times 10^{-6} \ \Omega \ cm^{-1}.
The polyvinylalcohol samples (PVA) were manufactured by Konam N.V., Amsterdam and by BUNA (GDR), the polyvinylpyrrolidon (PVP) samples by BASF. In Tables 1 and 2 the PVA and PVP samples are characterized by their average molecular weight and the acetate content [8]; for PVP cf. [10]. The polymer was added to \(10^{-2}\) M solution of dried potassium chloride. The polymer solutions were prepared according to a special formula described in [9]. In all experiments the time of adsorption was 8 h before the force measurements were begun. All measurements were performed in a climatized room at 295 K.

Results and discussion

We studied the steric hindrance of penetrating adsorbed polymer layers of homopolymers and copolymers. The PVP samples were commercial ones with a broad molecular weight distribution. It was shown that the molecular weight distribution becomes broader with increasing average molecular weight of the sample [10]. The polydispersity of the samples limits the theoretical interpretation of the experimental results. The average molecular weight is dependent on the method of measurement. For example, the average molecular weight of PVP K 90 was 933,000 from gel permeation chromatography (GPC) and 731,000 from the intrinsic viscosity. In the following we shall use the values calculated from the intrinsic viscosity.

The interaction energy-distance curves for PVP samples with different molecular weight are shown in Figure 1. The interaction energy per unit area is calculated with the Derjaguin approximation [17]. The data are shown in a semi-log plot to allow inclusion of the large variation in \(V(d)\) (for \(V\) cf. [2]). From Figure 1 it follows that in spite of the large differences in molecular weight of the samples, the shape of the curves and their ranges are not so different. In contrast to this, a bigger influence of the molecular weight was found for PVA samples [11] under comparable conditions. According to Cosgrove et al. [12] a higher fraction of PVP is bound at the quartz-solution-interface than PVA. This may be indicative of a different structure of the adsorbed layer.

The change of the free energy per unit area \(\Delta F\) between two macroscopic plane interfaces covered with a layer of adsorbed macromolecules can be calculated according to the HVO theory [5]. In this theory, the interaction energy is determined by the van der Waals attraction \(\Delta F_A\), the electrostatic repulsion \(\Delta F_E\) and the steric repulsion. The latter is split into a mixing term \(\Delta F_M\) and a volume restriction term \(\Delta F_{VR}\). Therefore the change of the free energy per unit area is

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\Delta F = \Delta F_M + \Delta F_{VR} + \Delta F_E + \Delta F_A.
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