Macromol. Symp. ***126,*** *51–64 (1997)*

MODIFICATION OF POLYMERS BY ADSORPTION PHENOMENA

Petra Weidenhammer and Hans-Jörg Jacobasch*

Institute for Polymer Research Dresden, P.O. Box 120411, 01005 Dresden, Germany

Abstract: The adsorption of ions and amphiphilic molecules on solid polymers is investigated by direct force measurements using an atomic force microscope (AFM). It is shown that electrolyte ions are changing the surface potentials of the solid polymers as well as their adhesive properties. The experiments show that the interaction with a negatively charged probe is dramatically decreased by the adsorption of anions. The adsorption isotherms are determined by zeta potential measurements (streaming potential of flat plates). In presence of adsorbing anions, the attractive interaction and the adhesion are reduced and can be eliminated completely.

So, even solutions of simple electrolyte ions can be applied intentionally in order to modify the interaction of polymer surfaces. A wide variety of technological applications becomes accessible.

INTRODUCTION

Solid polymer surfaces are subject to modification procedures in order to change their interfacial properties, i. e. their charge, the wettability by a given liquid phase or the adhesion toward another solid surface. In aqueous environments, adsorption of dissociated water and electrolyte ions, surfactants and polyelectrolytes plays an important role e. g. for the stability of colloidal dispersions. The interaction between charged solid bodies in

CCC 1022-1360/98/$ 10.00

aqueous solutions can be described by the DLVO theory. Additional effects like hydration repulsion or hydrophobic interaction have to be taken into account depending on the system [1]. The interaction and adhesion forces in a given system can be modified intentionally by adsorption of appropriate substances. For the investigation of technologically relevant phenomena, however, adsorption of e. g. organic contaminants is an undesirable circumstance, which diminishes the adhesive strength or the wettability. A further adsorbate, which is ubiquitous under ambient conditions, is water. Even on relatively hydrophobic polymer surfaces, a condensed water layer can be observed, which can give rise to capillary interaction and alters the van der Waals forces of the solid surface. This is particularly important for the interaction between two solid bodies at very small distances and in contact and therefore effects especially the adhesion forces considerably.

For this reason, experimental investigations about solid polymers in aqueous environments may also give some information about their behaviour in a "dry" state. In the present work, solid polymers are investigated by means of streaming potential and direct force measurements in aqueous electrolyte solutions.

Direct force measurements using a force measuring spring (see fig. 1) are realised in the Surface Forces Apparatus SFA [2], the Atomic Force Microscope AFM [3] and the MASIF apparatus [4, 5]. One surface is mounted on a spring with spring constant k, while the other one can be translated by a step motor or a piezo tube. Due to interaction forces between the two bodies, the spring is deflected from its rest position by an amount Δz and the force can be calculated using Hooke's law:

$$F = -k \cdot \Delta z \qquad (1)$$

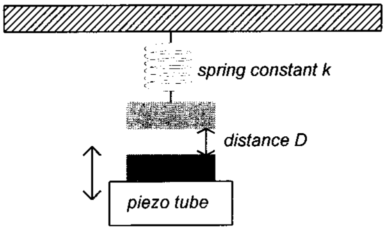

Fig. 1: Force measuring spring. The interaction between two solid surfaces causes a deflection of the spring. Spring constants are in the range of k = 0.1 N/m to 100 N/m. Forces as small as 1 nN can be measured using this type of setup.

EXPERIMENTAL

AFM and zeta potential measurements were performed on different solid polymers. In this paper, results from a technical high-performance poly(etheretherketone) (PEEK) are presented. The material was investigated by photoelectron spectroscopy (XPS) shown to contain no charged or dissociable groups on their surface [6]. The PEEK was cleaned with acetone before use in order to remove organic contaminants.

Standard silicon nitride cantilevers with integrated pyramidal tips were used as AFM probes. The length of the cantilever beams was 200 μm and 100 μm with a nominal spring constant of 0.12 N/m and 0.58 N/m, respectively. The tip radius is specified by the manufacturer to be 20 to 50 nm, but it is known that the radius may be as large as some hundred nanometers. The tips were irradiated with UV light for 15 minutes before use in order to remove organic contaminants.

All electrolytes and surfactants were analytical grade and used as received. The water was Milli-Q quality with a specific resistance of 18.2 MΩcm.

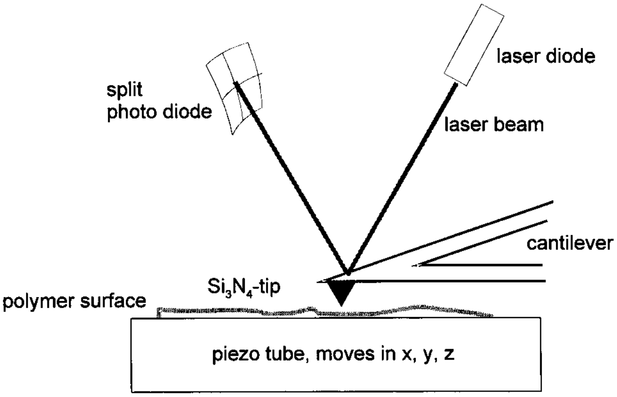

Fig. 2: AFM principle: a cantilever spring with integrated tip measures the force. The lateral (x-y) resolution of the measurement is better than 20 nm, the vertical (z) sensitivity lies below 1 nm.

Force measurements between the small probe and the samples were performed using a NanoScope III atomic force microscope (Digital Instruments, Santa Barbara, CA, USA) equipped with a fluid cell for the measurements in liquids. Probe and sample are then immersed in the solution. The sample is mounted on a piezoelectric tube and can be transduced in three dimensions. The probe is mounted on a cantilever spring, which is deflected by the action of forces between probe and sample. The cantilever deflection is recorded via the reflection of a laser beam on a split photo diode (fig. 2). For the force-distance measurements, the position of the sample in z direction is continuously varied. The cantilever deflection, which is proportional to the interaction force is recorded.

The zeta potential measurements were carried out using an Electrokinetic Analyzer EKA (Anton Paar KG, Graz, Austria) and a flat plate cell [7].

RESULTS AND DISCUSSION

Charging of solid surfaces by adsorption of electrolyte ions

Charge and potential of polymer surfaces in electrolyte solutions are investigated by streaming potential measurements. At a charged surface, an electrical double layer is built up, whose extension normal to the surface depends on the electrolyte concentration. If the solution is sheared relative to the solid surface, the "mobile" part of the double layer is separated from the "immobile" part and an electrical potential difference arises. The zeta potential is the potential of the shear plane relative to the bulk solution, which can be calculated from this value using the Helmholtz-Smoluchowski equation [8]. For the adsorptive processes investigated here and for low electrolyte concentrations, it has the same sign as the surface potential and can be regarded as a measure for the surface potential.

Surfaces, which do not have a native surface potential, e. g. dissociating *-COOH* groups, may still acquire a surface charge by preferential adsorption of one kind of ions from the electrolyte solution. This process is described by Stern's theory [9], which gives an equation connecting the zeta potential and the adsorption free energies of anions and cations:

$$\frac{\varepsilon}{4\pi\delta_0}(\psi_0 - \zeta) = \left[\frac{1}{1 + \frac{1}{c}\exp\left(\frac{\Phi_- - F\zeta}{RT}\right)} - \frac{1}{1 + \frac{1}{c}\exp\left(\frac{\Phi_+ + F\zeta}{RT}\right)}\right] \qquad (2)$$

ζ is the zeta potential, ψ_0 the surface potential, ε the permittivity, δ_0 the distance of the shear plane from the surface; Φ_- and Φ_+ are the anion and cation adsorption free energies, respectively, R the gas constant, T the absolute temperature and F Faraday's constant. Eq. 2 is valid for dilute solutions of 1:1 electrolytes.

The charging processes, which are taking place at the surface, can so be characterized by zeta potential measurements at varying pH or electrolyte concentration.

Fig. 3a shows a concentration dependent zeta potential curve of PEEK in KCl and KOH. It displays a negative zeta potential and therefore a negative acquired surface charge. The absolute zeta potentials reach a distinct extremum at a concentration of about 3 mmol/l, which can be attributed to a maximum coverage of the surface with ions due to specific adsorption processes. At higher concentrations, the absolute potential is decreasing, because the electrostatic attraction of counterions is dominating in this regime and diminishes the potential difference between surface and bulk solution. The position of the extremum can be calculated from eq. 2:

$$c_{\max} = \exp\left(\frac{\Phi_- + \Phi_+}{2RT}\right) \tag{3}$$

and

$$\zeta_{\max} = \frac{\Phi_- - \Phi_+}{2F} \tag{4}$$

and gives directly the adsorption free energies Φ_- and Φ_+, where. $c_{\max}$ and $\zeta_{\max}$ are the concentration and the zeta potential at the maximum position. Fig. 3b shows the zeta potential of the same polymer in Na_3PO_4 solutions of varying concentrations. In this case, a very broad extremum is observed at a much lower concentration. The values for the zeta potential are also much more negative than in KCl and KOH solutions, that means that also the surface potential is higher than for KOH and KCl. Eq. 2 cannot be used to calculate the adsorption free energy, since it is not applicable for 1:3 electrolytes, but a higher Φ_- can be assumed for PO_4^{3-} ions in comparison to Cl^- and OH^- ions.

Since the PEEK sample does not contain any dissociable groups on the surface, the charge must be due to preferential adsorption of electrolyte anions. It is well known that OH^- ions have a large adsorption free energy due to their high polarizability and their permanent dipole moment (in contrary to Cl^-). The large PO_4^{3-} anion possesses a very high polarizability and is even more likely to adsorb on a solid surface due to van der Waals forces. Probably, the ion's hydration shell is removed partially or completely during the adsorption process. This process is subject to further investigations.

The fact, however, that pure water contains OH^- ions in a concentration of 10^{-7} mol/l, must not be ignored either. In addition, if no precautions are taken in order to degas the water, there are also HCO_3^- and H_3O^+ ions present due to dissolved carbon dioxide from the air:

$$\begin{gathered} CO_2 + H_2O \leftrightarrow H_2CO_3 \\ H_2CO_3 + H_2O \leftrightarrow HCO_3^- + H_3O^+ \end{gathered} \tag{5}$$

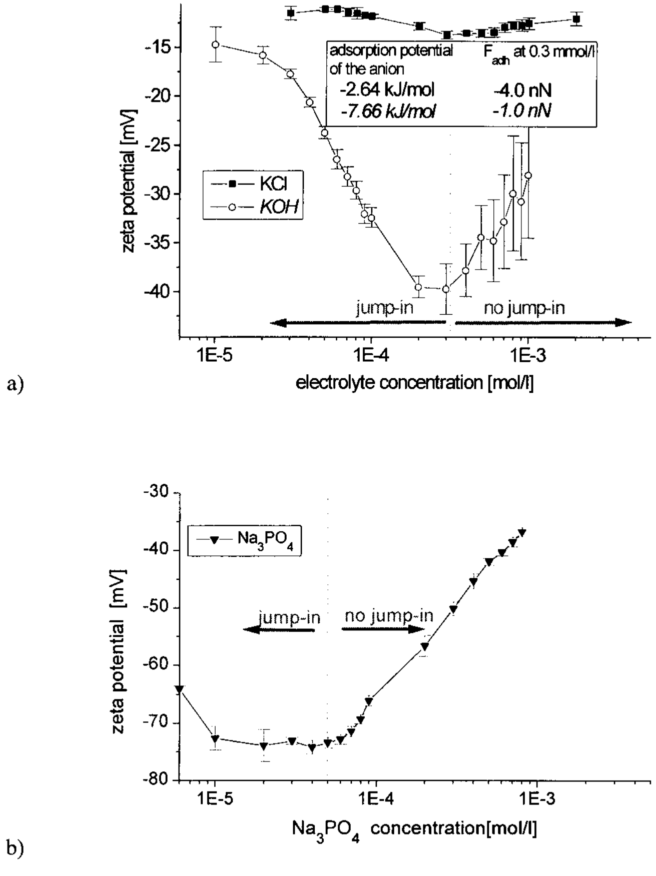

Fig. 3:

a) Zeta potential of PEEK in KOH and KCl solutions of varying concentration. The curves show that OH^- ions cause a higher acquired (negative) surface charge than Cl^- ions. The maximum of adsorption occurs at a concentration of about $3*10^{-4}$ mol/l. The inset displays the calculated adsorption free energies due to Stern's theory (see eq. 2 and the corresponding adhesion forces (see below).

b) Zeta potential of PEEK in Na_3PO_4 solutions of varying concentration. There is a broad extremum of adsorption occurring at a concentration of about $3*10^{-5}$ mol/l.

Consequently, even in pure water a certain surface potential arises due to autodissociation and adsorption processes. Especially in technologically relevant electrolyte solutions, this cannot be neglected.

Electrostatic interaction between dissimilar surfaces

In the atomic force microscope (AFM) experiments, the interaction between the solid surface and a small probe (see above) is investigated. In the present work, a silicon nitride tip was used. Its isoelectric point was shown to be $pH_{IEP} < 3$ [10] and it is therefore bearing a negative surface charge in neutral and alkaline solutions. The system can be approximated as a sphere with the tip radius *R*, which interacts with the flat sample. If the interaction takes place at constant surface potentials, the electrostatic force *F* at the distance *D* between the sphere and the flat plate is given by [11]:

$$F(D) = \pi \cdot R \cdot \varepsilon \cdot \kappa \cdot \left[\left(\psi_1^2 + \psi_2^2\right) \cdot \left(1 - \coth(\kappa \cdot D)\right) + 2 \cdot \psi_1 \cdot \psi_2 \cdot \operatorname{cosech}(\kappa \cdot D)\right] \qquad (6).$$

D is the separation distance, *R* the tip radius, ψ_1 and ψ_2 the surface potentials, κ the inverse Debye length and ε the electrical permittivity. The Debye length

$$\kappa^{-1} = \left(\frac{\sum_i z_i^2 e^2 \rho_{\infty i}}{\varepsilon \varepsilon_0 kT}\right)^{-\frac{1}{2}} \qquad (7)$$

depends on the bulk electrolyte concentration $\rho_{\infty i}$ (in units of m^{-3}) and determines the extension of the double layer. z_i is the valency of ion *i*, *e* the elementary charge, *k* the Boltzmann constant and *T* the absolute temperature. It gives a measure of how effectively the surface potential is screened by the ions in the solution. Since the surface charge is generated by the adsorption of ions from the solution, $\rho_{\infty i}$ controls the interaction of a solid polymer surface in two ways:

- The zeta potential ζ varies with the electrolyte concentration $\rho_{\infty i}$ and is determined by adsorption. The exact calculation of the surface potential ψ_1 requires a model for the electrical double layer, i. e. Stern's model [9].
- The Debye length decreases with increasing electrolyte concentration and sets the range of the electrostatic interaction.

The effects of varying surface potential are shown in fig. 4. Increasing surface potential leads to a higher repulsive interaction force and shifts the repulsive maximum to smaller distances. This effect is enhanced, if the electrolyte concentration increases at the same time, which follows from eq. 6 as well.

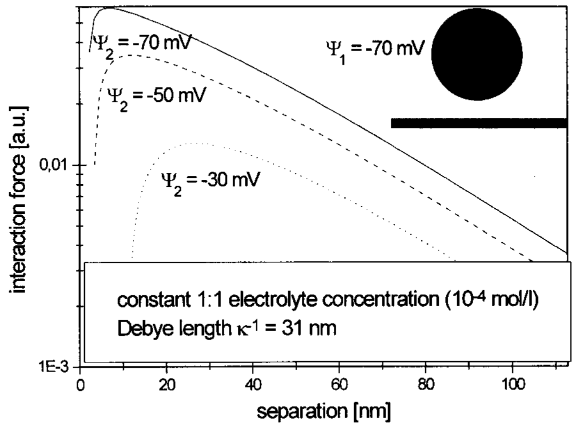

Fig. 4: The interaction force *F(D)* between two dissimilar surfaces and its dependence on the surface potential ψ_2 at constant electrolyte concentration.

Force distance measurements

Direct force measurements are employed here in order to measure the effect of the adsorption of electrolyte ions on solid surfaces. In the AFM, the total interaction force between the Si_3N_4 probe and a solid sample is measured. In aqueous solutions, the total force is the sum of the electrostatic forces and the van der Waals forces, which are both described in the DLVO theory. Additionally, structural forces such as hydrophobic or hydration interaction may act. Fig. 5 shows the typical long range electrostatic repulsion between charged surfaces (eq. 6). The electrostatic and van der Waals interaction are causing a repulsive maximum at small separations, which leads to a jump-into-contact due to a mechanical instability of the cantilever. In contact, the hard-wall repulsion between the electron shells of the surface atoms is observed, which can be described by a Lennard-Jones potential.

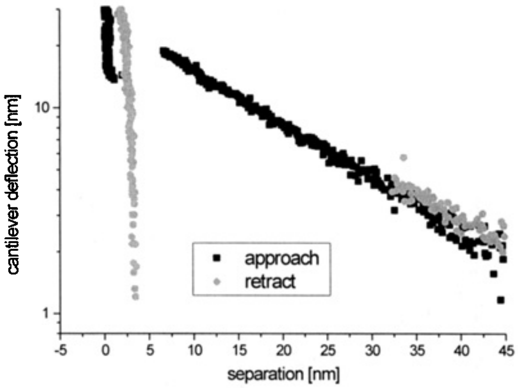

Fig. 5: A typical force-distance curve between a Si_3N_4 tip and the PEEK surface in 0.3 mM KCl solution. The long-range electrostatic interaction decays exponentially with the separation *D*, the measured Debye length of 16.1 nm is in good agreement with the theoretical prediction of 17.5 nm. The position of the repulsive maximum, which is described by eq. 6 and in fig. 4 can be obtained from this curve. The adhesion force can be calculated from the jump-out distance and the spring constant using Hooke's law (see eq. 1).

The double effect of varying electrolyte concentration on the force-distance curves between PEEK and Si_3N_4 in sodium phosphate solutions of varying concentration is shown in fig. 6. The electrolyte concentration was varied between 10^{-5} and 10^{-4} mol/l. With increasing concentration, the Debye length decreases according to eq. 7. At the same time, the surface potential of the PEEK surface is growing with increasing electrolyte concentration (see fig. 3b). This leads to changes in the height of the repulsive electrostatic barrier according to fig. 4. In contrast to Cl^- anions, phosphate anions are also adsorbing specifically on the Si_3N_4 tip [12] and therefore increasing its surface potential, which may give an additional contribution to the electrostatic interaction due to the change of both surface potentials.

Fig. 7 shows the results of a statistical analysis of a large number of force-distance curves measured between Si_3N_4 and PEEK in sodium phosphate solutions. The jump-in distance decreases with increasing concentration, which can also be seen in the typical force curves in fig. 6. The jump-in vanishes at a concentration of 10^{-4} mol/l and a pure repulsion is measured. The jump-out distance, which is proportional to the adhesion force, shows the same behaviour at this concentration. This means that there is no attractive interaction present between the probe and the polymer surface. Therefore, no contact hysteresis is observed and no adhesion force is measured either.

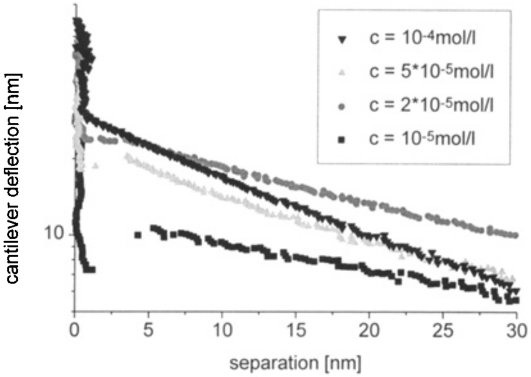

Fig. 6: Force-distance curves between a Si3N4 probe and PEEK in sodium phosphate solution. With increasing electrolyte concentration, the electrostatic interaction potential increases and the Debye length decreases.

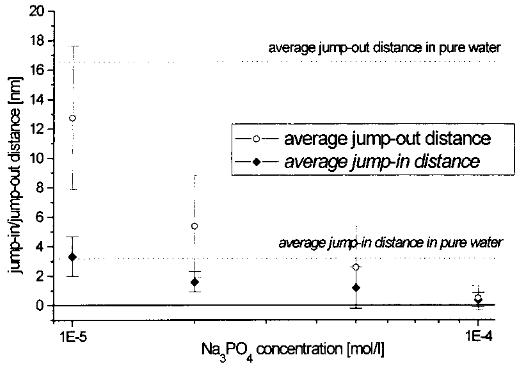

Fig. 7: Jump-in and jump-out distances between a Si_3N_4 tip and PEEK in Na_3PO_4 solutions of varying concentrations. The dotted lines show the values which were measured in pure water.

Adsorption and adhesion

The figs. 6 and 7 show that at a sodium phosphate concentration of 10^{-4} mol/l, no attractive interaction at all is observed. This effect was measured with different electrolyte solutions, when the anion possessed a strong adsorption potential towards the solid polymer surface. The experimental results imply that no "Born" contact can be established between the tip and the polymer surface. No adhesion force is measured in these cases. The concentration, at which this effect occurs, depends on the adsorbability of the respective anions. Fig. 8 shows the dependence of the measured adhesion force on the anion adsorption free energy. High adsorption free energy prevents adhesion at a lower electrolyte concentration. In the curve for the 0.3 mM solutions, the effect of decreasing attractive interaction at increasing surface charge (fig. 4) can be seen. For the phosphate anion, the attraction has already vanished at this concentration value, whereas in the 1 mM solutions, the attractive interaction disappeared also for the hydroxide and chloride ion.

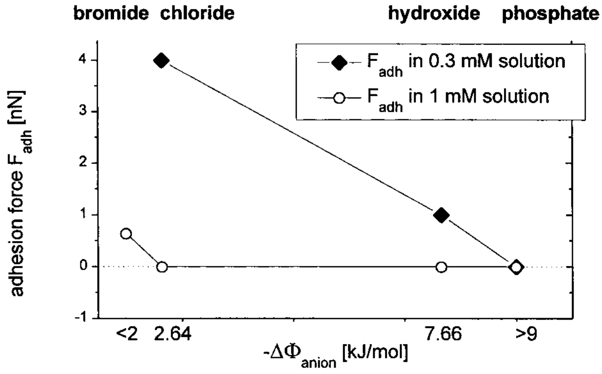

Fig. 8: Adhesion force in different electrolyte solutions. The adhesion force decreases with increasing anion adsorption free energy. The adsorption free energy values for chloride and hydroxide are to scale, the values for bromide and phosphate are estimates.

Regarding the DLVO theory, one would expect attractive van der Waals forces between the silicon nitride probe and solid polymers in an aqueous medium at small separations. Furthermore, the interaction forces at moderate electrolyte concentrations were well described by the assumption of electrostatic interaction at constant surface potentials. In order to fulfil the constant potential condition, the surface charges change continuously during the approach of the two surfaces. At the separation D, at which the condition

$$\psi_2 = \psi_1 \exp(\pm\kappa D) \tag{8}$$

is fulfilled, the sign of one surface charge changes and the interaction potential becomes attractive [11]. If the maximum of the adsorption isotherm is reached, the surface is covered with ions to the maximum extent and the lateral mobility of the ions is reduced remarkably. Under these circumstances, the assumption of electrostatic interaction at constant surface charges seems reasonable. Then the electrostatic force between two bodies with the same sign of surface charges is repulsive at all separations. Additionally, the adsorbed layer of ions of a finite size causes a shift of the plane of the surface potential with respect to the solid surface. Again, due to the diminished lateral mobility of ions, the interacting bodies cannot approach closer than twice the diameter of the adsorbed ions. This separation is too large for van der Waals forces to become important and the interacting surfaces do not reach „Born“ contact. In this case, no adhesion force is observed either, because an intimate contact is necessary for the formation of adhesive bonds. Fig. 9 a) shows a typical force curve between Si_3N_4 and PEEK in 0.5 mM KCl solution. The approach curve does not show a jump-in, which would exhibit a net attractive force. Obviously, no adhesive contact could be established, though a hard wall contact is reached. The force curve is completely reversible and does not show an adhesion hysteresis during the retraction of the tip.

The adhesion force, too, is changed by a variation of the electrolyte concentration. From many experiments, we can conclude: the longer the range of the attractive forces (during the approach), the stronger the adhesion. The range of the attractive forces is determined implicitly and explicitly by the amount of adsorbed ions on the solid polymer surface. Implicitly, the adsorbed ions are causing a certain surface potential, which governs the electrostatic part of the interaction (see above). Explicitly, the adsorbed ions are responsible for the interaction at very small distances, i. e. for the absence of the attractive interaction in 0.1 mM sodium phosphate solution (see fig.6).

A lack of attraction during the approach results in a completely reversible force-distance curve without any adhesion hysteresis. It is reported in the literature that the adsorbed layer can sometimes be displaced by exerting a higher loading force and its "thickness" can be determined by the resulting jump-in distance [13]. We were not able to observe this effect, though increasing the loading force.

A similar effect has been observed for the interaction between two polymer spheres in a surfactant solution. The surfactant is adsorbing on the surfaces and prevents polymer-polymer cohesion during contact, which occurs in pure water [14], and thereby reducing the attraction.

For a given solid polymer-electrolyte solution interface, the adhesion properties should be predictable from the adsorption characteristics of the solutes in the solution. Therefore, electrolytes and other water soluble molecules such as surfactants or polyelectrolytes can be used in order to modify the adhesion properties of a solid polymer deliberately.

CONCLUSIONS

Solid polymers can be charged in electrolyte solutions by the preferential adsorption of anions. Therefrom, an electrostatic surface potential arises, which depends on the bulk electrolyte concentration and changes the electrostatic contribution to the total interaction forces of the solid surface. This effect must not be neglected for solid polymers in electrolyte solutions and even in "pure" water. It depends on the kind of ions present in the solution and on their interaction with the solid polymer. It can also be utilised intentionally in order to modify the polymer surface properties.

The dissociation of water as well as adsorption processes in electrolyte solutions have to be taken into account if the interaction between solid bodies in aqueous environment is to be investigated, e. g. in flocculation processes. The adsorption of ions was seen to decrease the adhesion forces dramatically, it is even able to inhibit adhesion completely. In this case, the attractive van der Waals forces are overcome by the electrostatic repulsion due to ion adsorption on the surface. This means that for "real" systems, where the adsorption of third substances can weaken the interaction between two solid bodies by different mechanisms, van der Waals forces alone may be not be able to form an adhesive bond. If there are no adsorbing species present in a system, however, van der Waals forces are sufficient for establishing an adhesive bond, which causes a large pull-off force.

Due to the general presence of water in technological processes and its dissociation and the general presence of strongly adsorbing contaminants, adhesion forces can be weakened by the adsorption of water, ions and contaminants corresponding to their adsorption free energy. Real adhesion phenomena must then be considered as „competitive adsorption processes“.

Therefore, the aim of polymer modification must either be the prevention of strong adsorption processes or the creation of specific interaction with higher interaction energy than the adsorption energy of ions or contaminants. Furthermore, it can be concluded that the influence of electrolyte ions on adhesion phenomena of solid polymer surfaces can be described quantitatively using the results of zeta potential measurements.

ACKNOWLEDGMENTS

This work was supported by the DFG and the Max Buchner Foundation.

REFERENCES

[1] Israelachvili, J. N., *Surface and Interaction Forces*, San Diego 1992.

[2] Israelachvili, J. N., *Surface Science Reports* **14**, 109 (1992).

[3] Binnig, G., Quate, C. F., Gerber, Ch., *Phys. Rev. Lett.* **56**, 930 (1986).

[4] Parker, J. L., *Progr. Surf. Sci.* **47**, 205 (1994).

[5] Claesson, P. M.; Ederth, T.; Bergeron, V.; Rutland, M. W., *Adv. Colloid Interface Sci.* **67**, 119 (1996).

[6] Simon, F. et. al., *in preparation.*

[7] Jacobasch, H.-J., Simon, F., Werner, C., Bellmann, C., *Techn. Messen* **63(12)**, 439 (1996).

[8] Jacobasch, H.-J., *Oberflächenchemie faserbildender Polymerer*, Berlin 1984.

[9] Stern, O., *Z. Elektrochemie* **30**, 508 (1924).

[10] Weidenhammer, P. et. al., *unpublished results.*

[11] Hunter, R. J., *Foundations of Colloid Science Vol. I*, Oxford 1986.

[12] Hackley, V. A., Malghan, S. G., *Journal of Materials Science* **29**, 4420 (1994).

[13] Senden, T. J., Drummond, C. J., *Colloids Surfaces A* **94**, 29 (1995).

[14] Schmitt, F.-J. et. al., *in preparation.*