CROATICA CHEMICA ACTA CCACAA 48 (4) 463—479 (1976)

YU ISSN 0011-1643
CCA-952 541.183
Conference Paper

The Adsorption of Macromolecules on Solid/Liquid Interfaces

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The main problem in the investigations of polymer adsorption is clearing up the structure of the adsorbed layer, and the conformation of the adsorbed macromolecule. In order to get direct informations of the adsorbed macromolecule, calorimetric, ellipsometric and ir-spectrometric measurements are used. The structure of the polymer layer of the investigated polymer-solvent-adsorbens system is characterized by the adsorbed amount, the number of adhesive segments, the adsorption enthalpy and by the thickness and the concentration of the adsorbed layer. All this parameters are dependent on the structure of the macromolecule in solution, the degree of coverage of the adsorbent surface, the enthalpy balance and the surface density of the adhesive sites on the adsorbens. The reversibility of the adsorption is influenced by the conformation of the adsorbed macromolecule and by the molecular weight.

The adsorption of macromolecules on solids from solutions is not only of academic interest but also a basic phenomenon in various applied processes. For example: in the problems of the adhesion and cohesion of polymer layers and lacquers in the stability and viscosity of colloidal suspensions, in chromatography, especially the GPC of polymers, and last, but not least in some areas of biology, such as enzymatic reactions with carrier fixed enzymes, the structure and action of cell-membranes and the problems of manufacturing, finishing and administration of drugs (tablets, creames, lotions) and finally blood coagulation and replacement of blood.

The capability of the macromolecule to form multiple adsorption bonds because of its great number of equal adhesive segments and the internal flexibility of the segments distinguishes the adsorption behaviour of macromolecules from that of small molecules.

Extreme models for the conformations of adsorbed macromolecules based on these properties are:

1. The flat adsorbed macromolecules adhering with many segments in contact.
2. The macromolecule adsorbed in the form of a brush or bristle with only one or a small number of adhering segments at the end of the macro molecule.
3. The macromolecule adsorbed in loops with group of segments in the loop and group of segments in the bridge on the surface.

4. The macromolecule, adsorbed in coiled conformation with only a few segments, which maintains its form in the solution.

In order to describe the properties of low molecular adsorption systems, it is sufficient to determine the adsorption isotherms and their dependence on temperature and to calculate the isosteric Clausius Clapeyron enthalpy.

For macromolecular adsorption besides this, the structure of the adsorbed layer as well as the conformation of the adsorbed macromolecules are additional important criteria[1]. Therefore, representative parameters for the characterization of the structure are the thickness and the polymer concentration in the adsorbed layer, the number of adhesive segments of the macromolecule and the adsorption enthalpy. These quantities give important information about the conformation of the adsorbed macromolecule, about the binding enthalpy of the binding unit and about their influence on the irreversibility of polymer adsorption. These quantities are also of significance in applied processes. Some useful methods for the determination of these parameters are:

a) The thickness and the polymer concentration of the adsorbed layer is measurable by ellipsometry without presumptions[2–6]. Besides this method the thickness is also determinable by viscosity measurements in capillary systems, by changing the diameters of the capillary by adsorption and also by sedimentation measurements with small solid particles changing their hydrodynamic efficient diameter by the thickness of the adsorption layer[7–11].
b) In some cases the average number of adhesive segments and the number of contact points on the surfaces can be determined quantitatively. This is done by ir-spectrometric measurements of the absorption of the bands of the surface groups or of the adsorbed polymer, by changing their position by adsorption[4,12–20]. NMR-spectroscopy and EPR-spin-label spectroscopy have also been used[21–23].
c) It is possible to determine the number of adhesive segments and the binding enthalpy by direct calorimetric measurements of the adsorption- and immersion-enthalpies in combination with the adsorption isotherms and by comparing them with measurements of low molecular weight substances of the same chemical constitution[24,25].

It can be seen that the specific interactions between the adsorbent and polymer, the adsorbent and solvent, polymer and solvent and eventually between polymer and polymer compete energetically with each other and decide the adsorption behaviour, the conformation and the bond strength. Therefore, the investigation of the influence of these interactions by variation of the polymer-solvent-adsorbent system is of superior interest.

After this introduction the methods used will be shortly outlined and the experiments conducted and results obtained in some systems will be reported.

ELLIPSOMETRY

In the ellipsometry of thin layers, elliptic polarised light is reflected from a mirror which is the adsorbent (Cr, Au, Pt) (Figure 1)[5,6,26]. After the reflection the polarised state is changed from that of the incident light. This amplitude- and phase-change is based on the optical quality of the mirror.

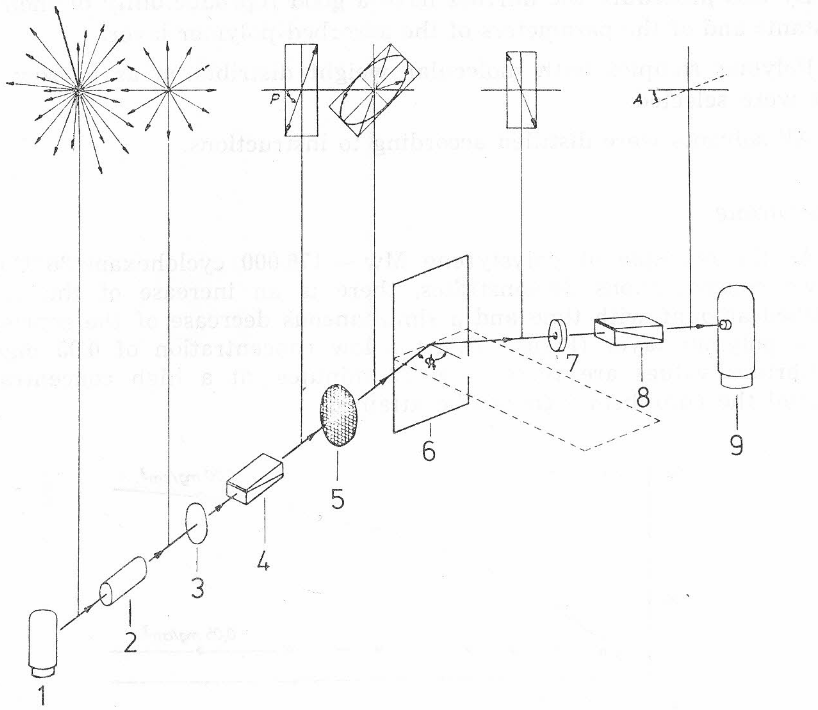

Figure 1. Schematic arrangement of the ellipsometer: light source (1), filter (2), collective lenses (3), polarizer (4), compensator (5), reflecting and adsorbing surface (6), aperture (7), analysator (8), phototube (9).

If adsorption occurs, an additional charge in the polarisation-state occurs; from this change one can calculate the refractive index and the thickness of the adsorbed layer.

The adsorption of the polymers (polystyrene, polyethylene glycol, polyvinylpyrrolidone and polymethylmethacrylate) discussed here was studied on chrome, gold and platinum mirrors, which are produced by high vacuum vapor-deposition with high optical planarity.

These mirror-adsorbents have several advantages:

1) Sharp, undiffused reflection of light because of their good planarity,
2) High intensity of the reflected light because of the high reflectivity.
3) Homogeneous flat surface because of using vapor-deposition.
4) Neglecting change of the optical constants in all solvents by oxydation and solution of surface layers with time.
5) Different adsorbability of the chrome mirrors because of the polar hydroxyl-surface-groups and the possibility of hydrogen-bonds in contrast to the gold- and platinum-mirrors.

The mirrors can be cleaned by a special procedure in chromosulfuric acid, at 35 ^{0}C, by washing in redistilled water, oxydation in the flame of a Bunsenburner and putting in a proper solvent.

By this procedure the mirrors have a good reproducibility of their optical constants and of the parameters of the adsorbed polymer layer.

Polymer samples with molecular weight distribution as narrow as possible were selected.

All solvents were distilled according to instructions.

Polystyrene

As the example of polystyrene Mw — 176 000 cyclohexane/36 °C/Chrome at two concentrations demonstrates, there is an increase of thickness and adsorbed amount with time and a simultaneous decrease of the concentration of the polymer layer (Figure 2). At a low concentration of 0.05 mg/ml the equilibrium values are reached in 30 minutes, at a high concentration of 5 mg/ml the equilibrium cannot be attained.

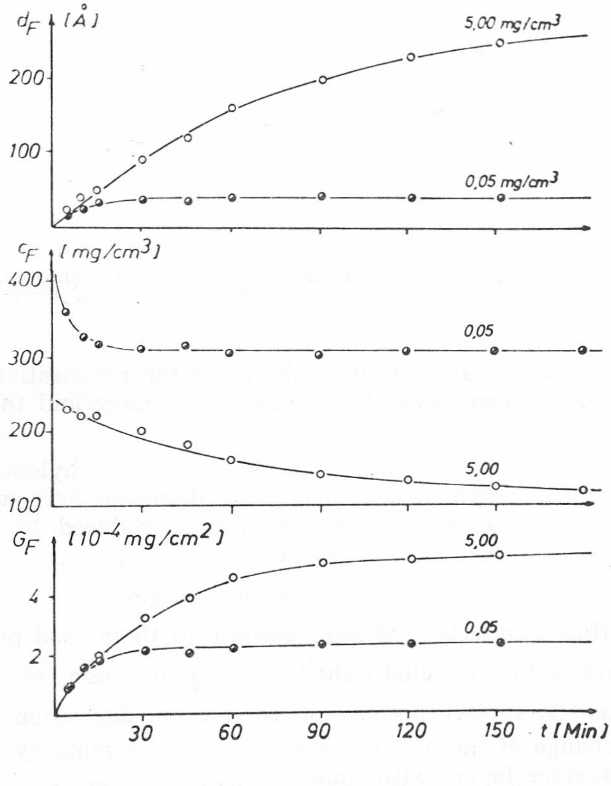

Figure 2. Thickness d_F, film-concentration c_F, adsorbed amount G_F *versus* time-polystyrene $M_W = 176000$ — chrome surface — cyclohexane — 36 °C — concentration of solution 0.05 mg/cm³ (●), 5.0 mg/cm³ (○).

The isotherms of polystyrene of different molecular weights show an increase in thickness and on the adsorbed amount and a decrease in the film concentration with increasing solution concentration (Figure 3).

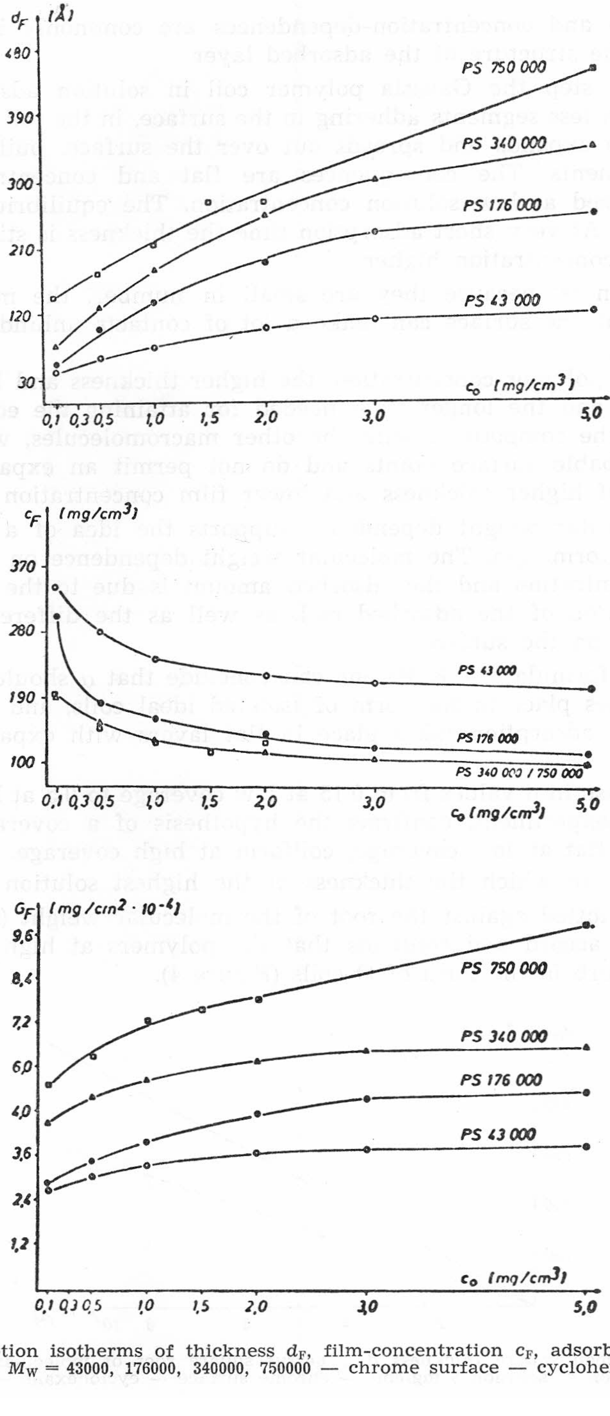

Figure 3. Adsorption isotherms of thickness d_F, film-concentration c_F, adsorbed amount G_F of polystyrenes $M_W = 43000, 176000, 340000, 750000$ — chrome surface — cyclohexane — 36 °C.

At the highest polymer-concentration the final saturation value is not reached.

The time- and concentration-dependences are commonly interpreted by a change in the structure of the adsorbed layer.

In a first step the Gaussia polymer coil in solution adsorbs diffusion controlled with less segments adhering to the surface, in the following step the macromolecule expands and spreads out over the surface, building up more adhering segments. The consequences are flat and concentrated polymer layers recognized at low solution concentration. The equilibrium is reached in 30 minutes. At very short adsorption time the thickness is still much lower and the film concentration higher.

The reason is: because they are small in number, the macromolecules which are near the surface can make a lot of contacts unhindered by other macromolecules.

At a high polymer concentration, the higher thickness and lower polymer concentration, and the longer time needed for attaining the equilibrium are attributed to the competition with the other macromolecules, which compete for the adsorbable surface points and do not permit an expansion process. Thus, layers of higher thickness and lower film concentration are obtained.

The molecular weight dependence supports the idea of a concentration dependent conformation. The molecular weight dependence on the thickness, the film-concentration and the adsorbed amount is due to the different size and conformation of the adsorbed coil, as well as the different number of contact points on the surface.

From the formula $d = K M^{\alpha}$ one can conclude that α should be 0.5 if the adsorption takes place in the form of isolated ideal coils, and that α should be zero if the adsorption takes place in flat layers with expanded polymer chains.

The increase in α values from 0.15 at low coverage to 0.5 at high coverage, found in the experiment, confirms the hypothesis of a coverage dependent conformation: flat at low coverage, coilform at high coverage.

The graph in which the thickness at the highest solution concentration (5 mg/ml) is plotted against the root of the molecular weight ($d_{\mathrm{rms}} = k \sqrt{M}$) shows a good accord and confirms that the polymers at high solution concentration adsorb in the form of Θ-coils (Figure 4).

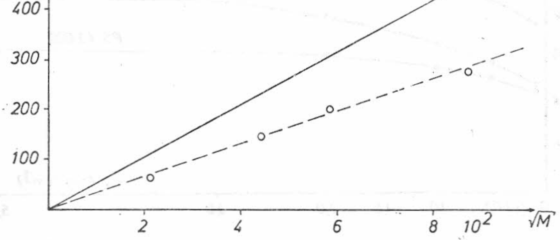

Figure 4. Root mean square thickness d_{rms} *versus* square root of molecular weight — concentration of solution 5 mg/cm^3 — chrome surface — cyclohexane — 36 °C.

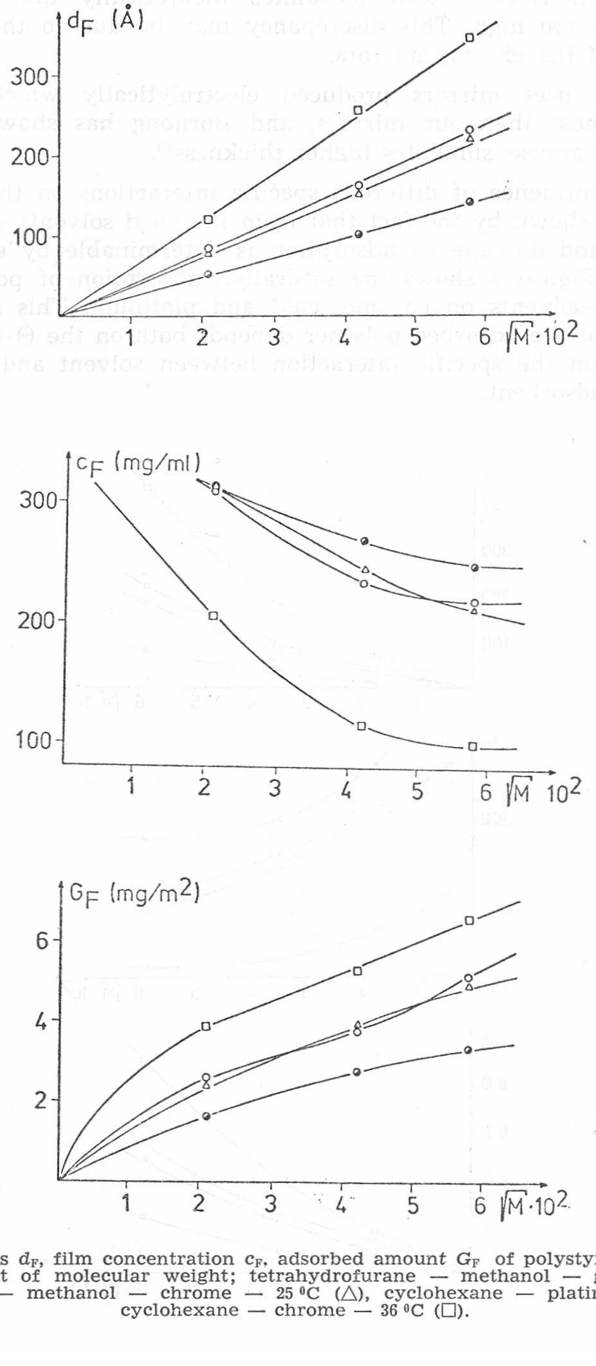

Figure 5. Thickness d_F, film concentration c_F, adsorbed amount G_F of polystyrene in saturation *versus* square root of molecular weight; tetrahydrofurane — methanol — gold — 26 °C (●), tetrahydrofurane — methanol — chrome — 25 °C (△), cyclohexane — platinum — 36 °C (○), cyclohexane — chrome — 36 °C (□).

Stromberg's straight line[3] is steeper than that found by us. This is in agreement with Hoeve[28] who postulates theoretically that the values of Stromberg are too high. This discrepancy may be due to the difference in the surfaces of the chrome mirrors.

Stromberg uses mirrors produced electrolytically which have higher surface roughness than our mirrors, and Bornong has shown theoretically that higher roughness simulates higher thickness[29].

That the influence of different specific interactions on the adsorption is very strong is shown by the fact that from the good solvents such as methylethyl ketone and dioxane no adsorption is determinable by ellipsometry[26,27]. Furthermore, Figure 5 shows the saturation adsorption of polystyrene from some other Θ-solvents on chrome, gold and platinum. This shows that the conformation of the adsorbed polymer depends both on the Θ-conformation in solution, and on the specific interaction between solvent and adsorbent and polymer and adsorbent.

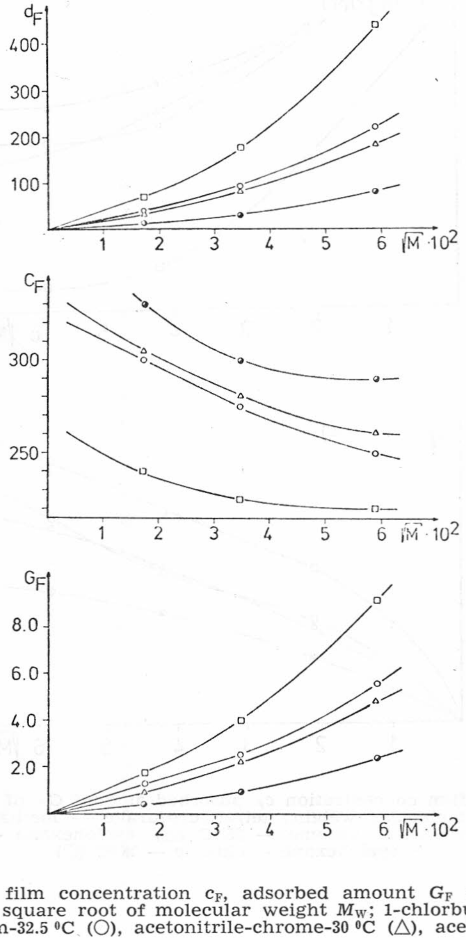

Figure 6. Thickness d_F, film concentration c_F, adsorbed amount G_F of polymethylmethacrylate in saturation *versus* square root of molecular weight M_W; 1-chlorbutane-chrome-32.5 °C (□), 1-chlorobutane-platinum-32.5 °C (○), acetonitrile-chrome-30 °C (△), acetonitrile-gold-30 °C (●).

Polymethylmethacrylate

This is also valid for polymethylmethacrylates in Θ-systems, which are shown in Figure 6. This Figure also shows the specific influence of specific interactions. Further investigation, especially calorimetric measurements of solution-, dilution-, immersion- and adsorption-enthalpies, will be necessary to determine which influence is the dominant one for conformation.

In contrast to the concentration-behaviour of polystyrene polymethylmethacrylate shows that thickness, the adsorbed amount and film concentration increase parallel with solution concentration (Figure 7).

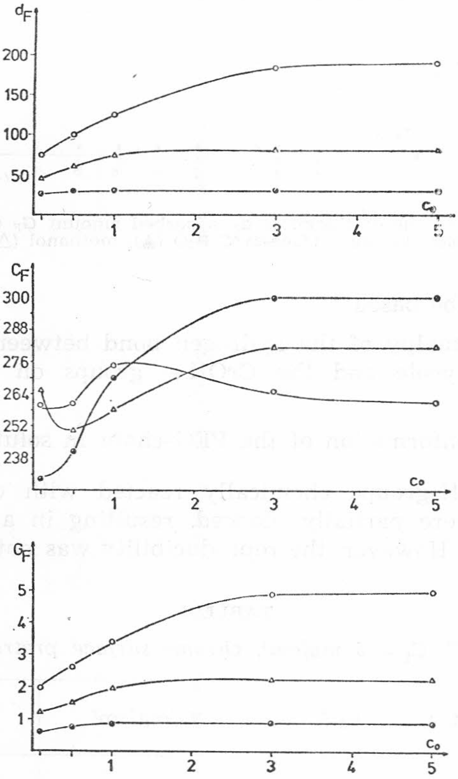

Figure 7. Adsorption isotherms of thickness d_F, film concentration c_F, adsorbed amount G_F of polymethylmethacrylates $M_W = 30000$ (●), 121000 (△) 352000 (○)-chrome surface-acetonitrile 30 °C.

In this system the coverage-dependent conformation is not remarkable, because the simultaneous increase in thickness and film concentration may be due only to the filling up effect of the polymer layer.

Polyethyleneglycol

In contrast to polystyrene and polymethylmethacrylate, polyethyleneglycol adsorbs in the whole coverage-range in flat expanded conformation with a thickness less than 20 Å (Figure 8) on chrome surfaces[6]. The calculated refractive index of the layer, n = 1.48, corresponds to the refractive index of the pure solid polymer. This means, that a layer of a thickness less than 20 Å, only pure polymer without solvent adsorbs.

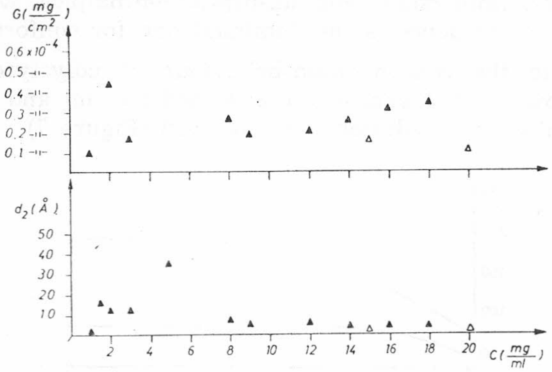

Figure 8. Adsorption isotherms of thickness d_2, adsorbed amount G_F of polyethyleneglycol M_W 40000-chrome surface-25 °C-H_2O (▲), methanol (△).

This flat layer may be based:

a) on the higher enthalpy of the hydrogen bond between the ether-segments of polyethyleneglycole and the CrOH— groups on the chrome-surface, and

b) on a stretched conformation of the PEG-chain in solution (especially H_2O).

When the CrOH-groups chemically reacted with dimethyldichlorsilane the CrOH-groups were partially blocked, resulting in a higher thickness of the adsorbed layers. However, the reproducibility was not very good (Table I).

TABLE I

PEG 40 000, H_2O 25 °C, $C_L = 5$ mg/cm³, chrome-surface pretreated with $SiCl_2(CH_3)_2$

Experiment	d_2/Å	G/mg/cm²	n_2
1	161	$7.70 \ 10^{-5}$	1.3408
2	415	$8.40 \ 10^{-5}$	1.3364
3	142	$1.10 \ 10^{-4}$	1.3455
4	167	$1.75 \ 10^{-4}$	1.3498
5	401	$1.00 \ 10^{-4}$	1.3367

The reduction of the number of binding groups on the surface reduces the possibility for polymer segments to adsorb in direct sequences with many contact points. The probability of loops becomes higher, resulting in a higher layer-thickness and smaller film concentration.

Polyvinylpyrrolidone

Despite the possibility of forming hydrogen bonds polyvinylpyrrolidone adsorbs at the same solution concentration in layers of higher thickness 350—450 Å with smaller film concentrations (Figure 9).

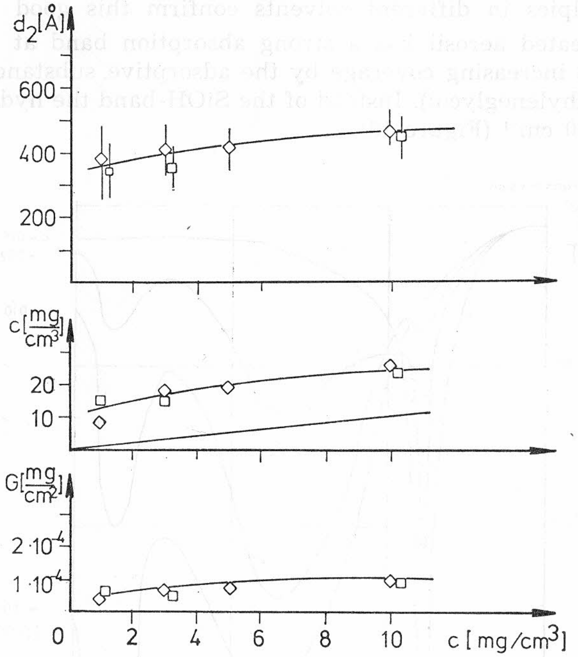

Figure 9. Adsorption isotherms of thickness d_2, film concentration c_F, adsorbed amount G_F of polyvinylpyrrolidone K 90 -chrome surface-25 °C-H_2O — one chrome mirror (◇), different chrome mirrors (□).

This behaviour may be ascribed to a number of reasons:

a) different binding enthalpies due to the sterically higher binding distances,
b) different solvation-interaction with the solvent,
c) different structure in solution due to the solvation interaction,
d) eventually higher polymerisation degrees of the samples of PVP (=-polyvinylpyrrolidone) and the broader molecular weight distribution.

Ir-SPECTROSCOPY

The ir-spectrometric measurements of the numbers of adhesive segments require adsorbents of high specific surface area with high numbers of adsorptive surface groups which can produce sufficient quantitatively analysable effects[20,25]. Therefore, the pyrogenic silicon dioxid aerosil with a specific area of 200 ± 25 m^2/g was used. Since its surface is very smooth and nonporous it is useful as a model-adsorbent. This is demonstrated by electron microscopy, which also shows that the primary particles of 120 Å in diameter form big aggregates in flock form. The surface dimensions of these particles are greater than those of the adsorbed macromolecule.

The aerosil is heated to 300 °C in vacuum at 0.1 Torr for five hours and then immediately wetted with the solvent, carbontetrachloride, and subjected to ir-experiments or placed into ampules under nitrogen and melted.

This pretreatment gives well reproducible surfaces, which have the optimum density of hydroxyl groups demonstrated by ir-measurements. The wetting enthalpies in different solvents confirm this good reproducibility[25].

The pretreated aerosil has a strong absorption band at 3695 cm^{-1} which decreases with increasing coverage by the adsorptive substances, especially by PEG (= polyethyleneglycol). Instead of the SiOH-band the hydrogen bond-band appears at 3300 cm^{-1} (Figure 10).

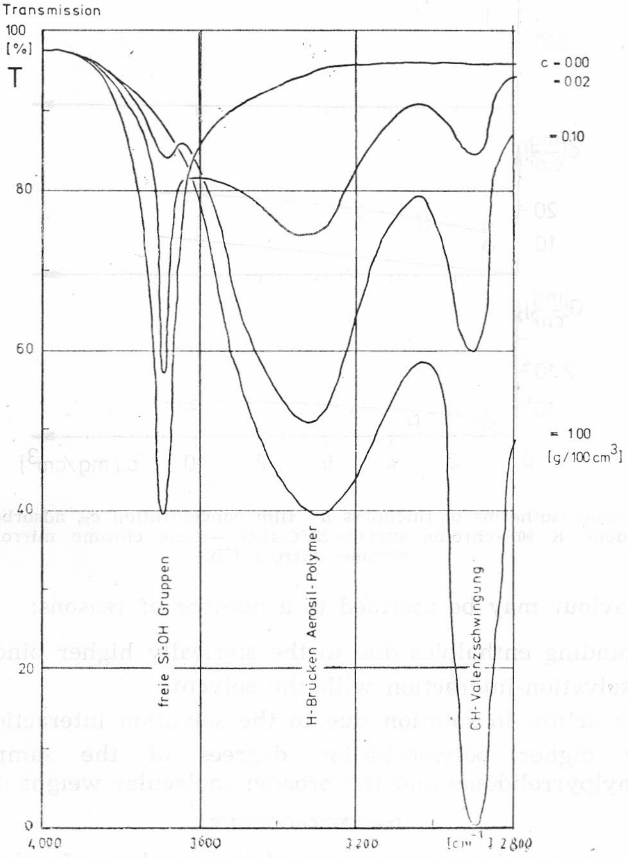

Figure 10. Ir-spectrum, polyethyleneglycole M_w 6000 — CCl_4 — Aerosil 200 — 25 ° at polymer concentrations c = 0.0—0.02—0.1—1.0 g/100 cm^3.

For purposes of comparison we adsorb on aerosil PEG of different molecular weight and ethyl glycol, ethyl alcohol, diethyl ether and ethyleneglycoldiethylether.

The adsorbed amount and the adsorption isotherms are determined from the concentration difference between the concentration of the solution in equilibrium and the initial weighed concentration. Some isotherms are given in Figure 11.

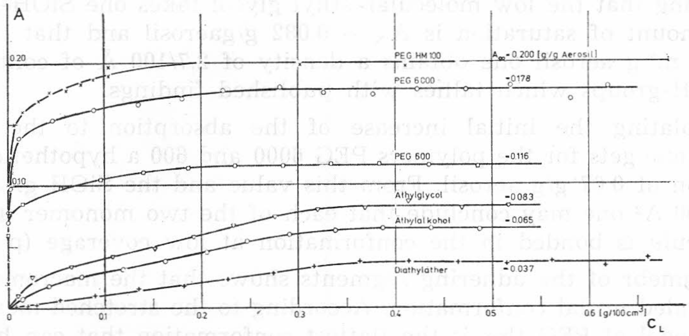

Figure 11. Adsorption isotherms of adsorbed amount *A* of polyethylene-glycols M_W 40000, M_n 6000, M_n 600, ethyl glycol, ethanol, diethylether — CCl_4 — Aerosil 200 — 25 °C.

The concentration in solution is measured with ir at the CH-valence vibration at 2900 cm^{-1}. Remarkable is the steep rise of the isotherms, demonstrating the high adsorption affinity of polymer adsorption.

In Figure 12 the extinction of the hydrogen bonds responsible for the adsorption is plotted against the adsorbed amount. The curve obtained is convex. This means that with higher coverage the extinction increases in smaller quantities. At saturation the extinction of PEG and of ethyl glycol are equal within the error limits.

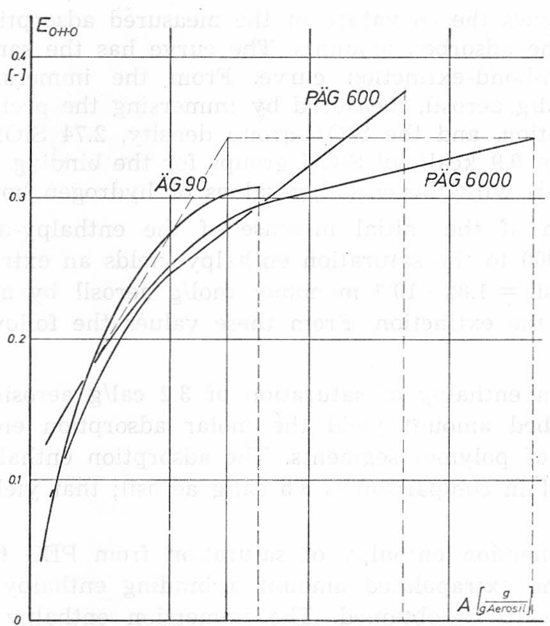

Figure 12. Extinction E_{O-H-O} of the hydrogen bonds at 3300 cm^{-1} *versus* adsorbed amount of polyethyleneglycols 6000, 600 and ethyl glycol — CCl_4 — 25 °C — aerosil 200.

This means that the number of the hydrogen bonds is almost equal in saturation.

Supposing that the low molecular ethyl glycol takes one SiOH-group, and that the amount of saturation is $A_\infty = 0.082$ g/gaerosil and that the specific area is 200 m^2/g aerosil one obtains a density of 2.7/100 Å of contact groups and of SiOH-groups which tallies with published findings.

Extrapolating the initial increase of the absorption to the saturation absorption, one gets for the polymers PEG 6000 and 600 a hypothetical amount of saturation of 0.07 g/g aerosil. From this value and the SiOH group density 2.7 SiOH/100 Å^2 one may conclude that each of the two monomer units of the macromolecule is bonded in the conformation at low coverage ($p = 0.5$).

This numebr of the adhering segments shows that the macromolecule has a flat expanded initial conformation. According to the stretched meander-form molecule model of PEG this is the flattest conformation that can be obtained — the binding of all ether units is not possible because of sterical reasons.

From the convex curvature of the extinction one can conclude that with increasing coverage this extremely high number of adhering segments decreases. The most expanded conformation goes over in a less smooth conformation. But also in saturation, on the average, one of four segments must be bonded.

CALORIMETRY

The exothermic immersion- and adsorption- enthalpies for the same polymer-solvent-adsorbent-system are determined directly by using an isoperibolic microcalorimeter[24,25].

Figure 13 shows the curvature of the measured adsorption enthalpies in dependence on the adsorbed amounts. The curve has the same characteristic as the hydrogen-bond-extinction curve. From the immersion enthalpy in saturation, 9.0 cal/g aerosil, measured by immersing the pretreated aerosil in the polymer-solution, and the SiOH-group density, 2.74 SiOH/100 Å^2 on the surface a value of 9.9 kcal/mol SiOH groups for the binding enthalpy results. This value accords with the enthalpy-values of hydrogen bonds.

Extrapolation of the initial increase of the enthalpy-adsorbed amount curve of PEG 6000 to the saturation enthalpy yields an extrapolated amount of 0.08 g/g aerosil $= 1.82 \cdot 10^{-3}$ monomer mol/g aerosil by analogy with the extrapolation of the extinction. From these values the following conclusions can be made:

a) The adsorption enthalpy of saturation of 3.2 cal/g aerosil and the extrapolated adsorbed amount yield the molar adsorption enthalpy of PEG: 1.76 kcal/mol of polymer segments. The adsorption enthalpy of saturation of ethyl glycol in comparison is 3.5 cal/g aerosil; that yields 3.94 kcal/mol ethyl glycol.

b) From the immersion enthalpy of saturation from PEG 6000 of 9.0 cal/g aerosil and the extrapolated amount a binding enthalpy of 4.9 kcal/mol polymer segments is obtained. The immersion enthalpy of ethyl glycol yields a binding enthalpy of 10 kcal/mol of ethyl glycol in agreement with the binding enthalpy of 9.9 kcal/mol of SiOH-binding sites.

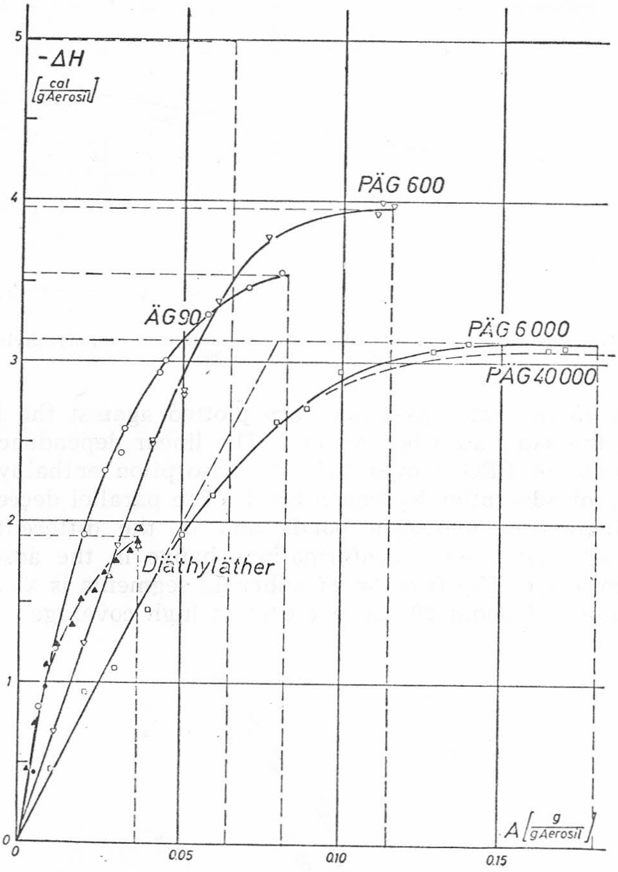

Figure 13. **Adsorption enthalpy — ΔH *versus* adsorbed amount A of polyethyleneglycols 40000, 6000, 600, ethylglycol and diethylether — CCl_4 — 25 °C — Aerosil 200.**

Both considerations point to a fraction of $p = 0.5$ attached polymer segments of a polymer chain which is in full agreement with the conclusion from the ir-results. One can conclude from the adsorbed amount and the measured adsorption enthalpy, as well as from the ir-spectrometry that the fraction of adsorbed segments is about $p = 0.2 — 0.25$ in the saturation region. This means that the polymer chain must be adsorbed in extreme flat conformation in all coverage regions.

This fact is confirmed by the ellipsometric thicknesses on chrome which are smaller than 20 Å in the whole coverage region (Figure 8). Further confirmation is provided by the extremely small dependence of the adsorbed saturation amounts on the molecular weights of PEG (Figure 14). From the theoretical point of view in this plot the slope of log adsorbed amount against log molecular weight should be zero if a flat adsorption layer exists without changing the conformation.

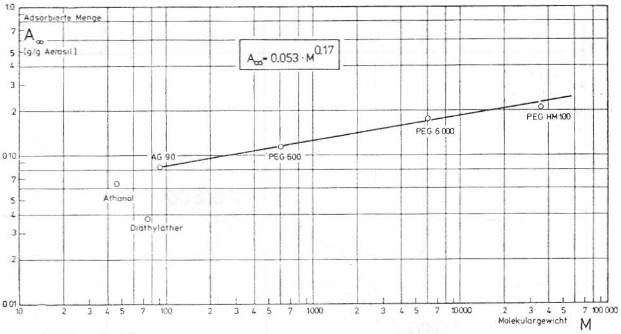

Figure 14. Molecular weight dependence of saturation amounts of polyethyleneglycols — CCl_4 — 25 °C — aerosil 200.

In Figure 15 the enthalpy-values are plotted against the hydrogen-bond absorption at the same adsorbed amount. The linear dependence for different molecular weight of PEG proves that the adsorption enthalpy is a measure of the number of adsorptive hydrogen bonds. The parallel decrease in the differential extinction of hydrogen bonds and in the differential adsorption enthalpy is explainable by a conformation change in the adsorbed polymer chains with coverage. The fraction of adhering segments is about 50 per cent at low coverage and about 20—50 per cent at high coverage.

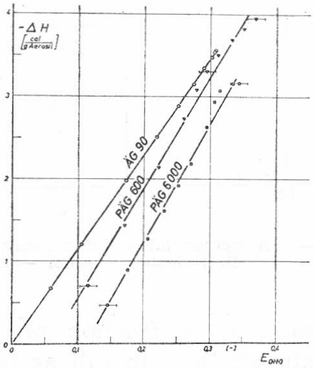

Figure 15. Adsorption enthalpies — ΔH *versus* extinction E_{O-H-O} of the hydrogen bonds of polyethyleneglycols — CCl_4 — 25 °C — aerosil.

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SAŽETAK

Adsorpcija makromolekula na međufazi kruto/tekuće

E. Killmann

Osnovni je problem pri ispitivanju adsorpcije polimera rješenje strukture adsorbiranog sloja, odnosno konformacije adsorbiranih makromolekula. Podaci o konformaciji adsorbiranih molekula dobiveni su kalorimetrijskom, elipsometrijskom i i.r.-spektrometrijskom metodom. Struktura polimernog sloja u sistemu polimer-otopina-adsorbens, karakterizirana je količinom adsorbensa, brojem adhezivnih segmenata, adsorpcijskom entalpijom te debljinom i koncentracijom adsorbiranog sloja. Ti parametri ovise o stupnju pokrivenosti površine adsorbensa, ravnotežnoj entalpiji, strukturi makromolekula u otopini i o površinskoj gustoći mjesta adhezije na adsorbensu. Reverzibilnost adsorpcije ovisi o konformaciji adsorbirane makromolekule i o njezinoj molekularnoj težini.

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