

Microcalorimetric studies of the adsorption of N-ethylpyrrolidone, oligomeric and polymeric vinylpyrrolidone from CHCl_3 on silica^{*})

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Abstract: Adsorption enthalpies of N-ethylpyrrolidone, oligomeric and polymeric vinylpyrrolidone from CHCl_3 solution on silica interfaces (Aerosil 200) have been measured at 25 °C by microcalorimetry. The dependence on surface coverage has been examined using measured adsorption isotherms. Binding enthalpies are calculated with fractions of adhered segments obtained by IR spectrometry and wetting enthalpies received from calorimetry. Fractions of adhered segments are derived from the adsorption enthalpies assuming equal binding enthalpies of monomers and polymer segments and considering desorption enthalpies of the solvent depending on the surface area of the polymer segments. The resulting enthalpies are compared with literature values from other solvents and the incongruity of the fraction of adhered segments obtained by IR, ESR, NMR and microcalorimetry is explained.

Key words: polymer adsorption, microcalorimetry, enthalpy of adsorption, fraction of adhered segments, silica

Introduction

For the occurrence of adsorption of macromolecules all theories [1-5] demand the existence of a defined adsorption enthalpy beyond a critical value. The conformation of the adsorbed polymers and the distribution of segments in the adsorbed layer perpendicular to the surface of the adsorbent are decisively influenced by the free enthalpies of the polymer-adsorbent and the polymer-solvent interactions. Until now, microcalorimetric measurements of the adsorption enthalpies have been a possible means of investigating the energetics of the polymer adsorption [6-10].

Knowing the adsorption enthalpy per adsorbed segment and the adsorption isotherm it is possible to determine the fraction of adhered segments from the adsorption enthalpy, also in cases where no specific interactions of polymer- and surface groups take place and spectroscopic methods (IR, NMR, ESR) fail.

Recently the free enthalpy of adsorption has been determined by displacement measurements with adsorptives ("displacers"), competing with the adsorbed polymer segments [11, 12].

In this study the integral adsorption enthalpy of a polymeric vinylpyrrolidone (PVP), an oligomeric vinylpyrrolidone (OVP) and the monofunctional model adsorptive N-ethylpyrrolidone (NEP) on silica (Aerosil 200) in CHCl_3 suspension, dependent upon the adsorbed amount, and the wetting enthalpy of the adsorbent Aerosil 200 in the solvent CHCl_3 have been determined by microcalorimetry. The specification of the substances and their pretreatment has been reported in a preceding publication [13, 22].

Measuring technique

An isoperibolic calorimeter "LKB 8700-1 Precision Calorimetry System", LKB-Produkter AB, Stockholm-Bromma 1, Sweden, was used. After adding adsorptive solution step by step, the heat developed during adsorption was measured at 25 °C. To correlate the adsorption enthalpies with the amount adsorbed adsorption isotherms were determined. Measuring device and measuring procedures to determine the adsorption enthalpies had been described by Winter [14] and by Korn [15].

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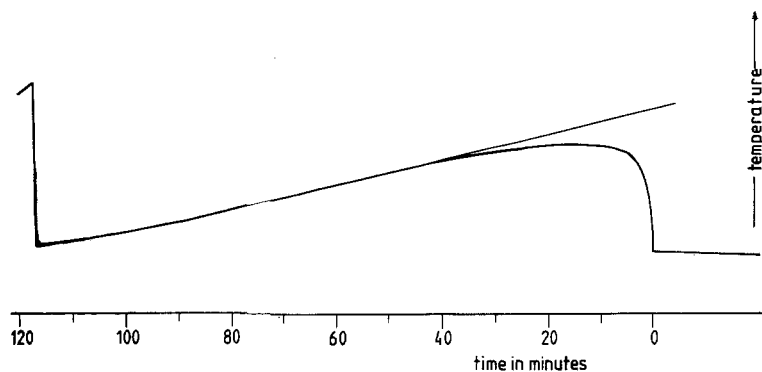


Fig. 1. Temperature as function of time of adsorption; addition of PVP/ CHCl_3 solution to precovered Aerosil suspension; ($A = 3.8 \cdot 10^{-6} \text{ mol m}^{-2}$ Aerosil; $t = 0$: break of the ampoule with 0.8 ml PVP solution ($7.2 \cdot 10^{-4} \text{ mol}$); $t = 118 \text{ min}$: electrical calibration)

The reported ampoule technique proves to be disadvantageous in two respects. To insert a new ampoule the calorimeter vessel has to be opened and the start temperature has to be readjusted; this is a time-consuming operation. Because of the small volume of the ampoule (1 ml) and the limited solubility of the adsorptive only relatively small changes in concentration can be obtained. By reconstructing the LKB-calorimeter and using it in titration mode, the disadvantages can be avoided.

The solution is supplied through a capillary tube into the calorimetric vessel with the help of a motor burette (Multi Dosimat 645, Metrohm, Herisau). Before its addition, the adsorptive solution is thermostated in a thin teflon tube in the main thermostat of the calorimeter. Using this titration device the adsorptive solution can be added in one step or in several steps. A concentration change ten times greater than with the ampoule technique can be obtained if a volume of 10 ml of the adsorptive solution (volume of the supplying teflon tube in the thermostat) is admitted.

An Aerosil concentration of 10 g l^{-1} was chosen to guarantee a good mixture in the calorimeter vessel. In order to measure the wetting enthalpies 23 to 74 mg of Aerosil 200 were weighed into ampoules for solids (1 ml, LKB) and heated 3 hours at 300°C in vacuum in a heating apparatus described by Eckart [6]. After annealing the ampoules were melted under nitrogen. Breaking the ampoules in the calorimetric vessel, the silica is wetted by CHCl_3 and the resulting enthalpies are measured.

The calorimeter used is suitable for measurements requiring up to 10 minutes. Under favorable conditions (negligible fluctuations in temperature — time plot before and after the experiment) enthalpy measurements could be accomplished for reactions taking one hour or even longer with sufficient accuracy (fig. 1). Results from such lengthy experiments, adding polymer solution of high molecular PVP to a silica suspension already partly covered, demonstrate that the adsorption process and the corresponding production of heat lasts more than 30 minutes.

Results

Integral adsorption enthalpy

The integral adsorption enthalpy $\Delta H(\theta)$ is obtained according to equation (1) from the heat measured, ΔH_{meas} , produced by the addition of polymer solution to a standard pretreated Aerosil suspension [13] con-

sidering the dilution heat, ΔH_d , in the corresponding experiment, adding the polymer solution to the solvent without Aerosil.

$$\Delta H(\theta) = \Delta H_{\text{meas}} - \Delta H_d \quad (1)$$

The exact analysis of the process taking place in the calorimeter shows that in addition to the dilution enthalpy, ΔH_d , an enthalpy contribution has to take into account, which is related to the dilution during the adsorption process itself. Calculations show that under the experimental conditions used this additional enthalpy contribution is negligible in comparison to the measured enthalpy and the ΔH_d -value [22].

In figures 2, 3 and 4 the values of ΔH_{meas} , ΔH_d and $\Delta H(\theta)$ are represented in dependence of the dosage concentration. NEP (fig. 2) shows in contrast to OVP (fig. 3) and PVP (fig. 4) a negative dilution enthalpy corresponding to an exothermic dilution. The dependences of the adsorption enthalpies on the amount adsorbed are demonstrated in figure 5. At high amounts adsorbed PVP shows a convex trend with a smaller increase of the adsorption enthalpies compared with the amounts adsorbed. The reproducibility of the measured enthalpies is better than $\pm 5\%$.

Wetting enthalpy

The wetting enthalpy is determined by breaking an ampoule, filled with standard preconditioned Aerosil, in the solvent presented in the calorimetric vessel. The enthalpy of evaporation of the solvent into the volume of the ampoule has to be considered as a correction value. Figure 6 shows the measured heats ΔH_w as function of the amount of silica weighed in. From the negative intercept of the ordinate results an evaporation enthalpy of 0.49 J for the 1 ml ampoule. The slope

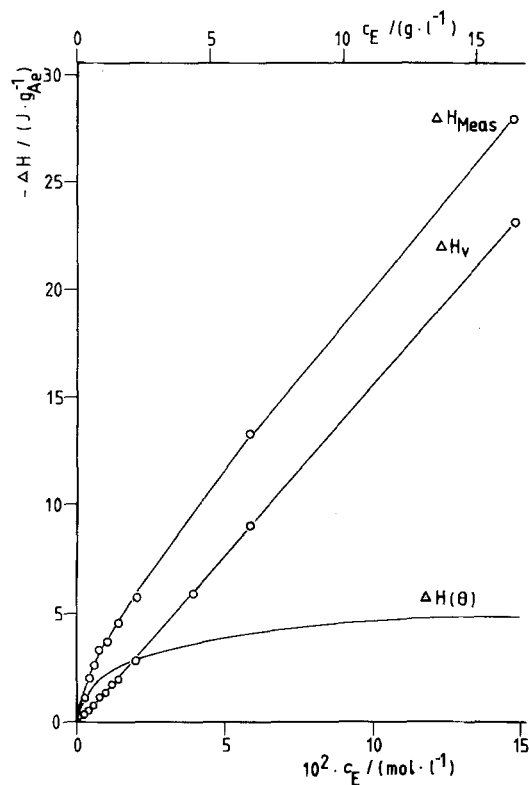


Fig. 2. Measured enthalpy, ΔH_{Meas} dilution enthalpy, ΔH_v , and integral adsorption enthalpy, $\Delta H(\theta)$, as function of the adsorptive concentration, c_E ; system: NEP, CHCl_3 , Aerosil 200, $c_s = 10 \text{ g l}^{-1}$

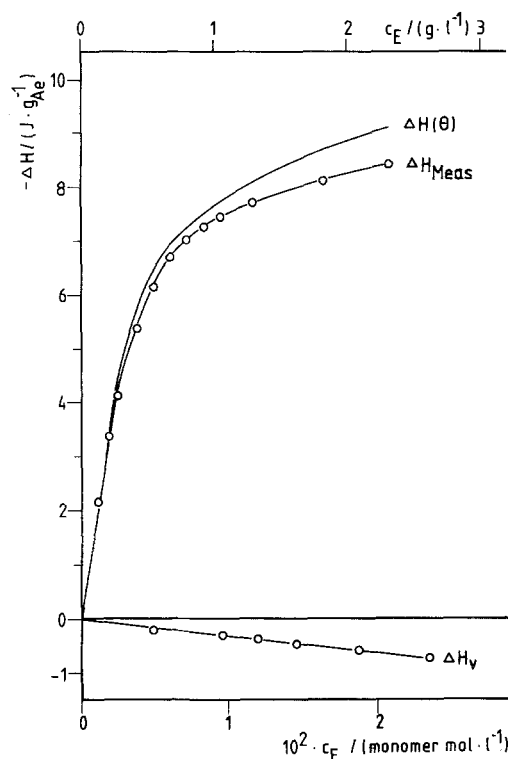


Fig. 3. Measured enthalpy, ΔH_{Meas} dilution enthalpy, ΔH_v , and integral adsorption enthalpy, $\Delta H(\theta)$, as function of the oligomer concentration, c_E ; system: OVP, CHCl_3 , Aerosil 200, $c_s = 10 \text{ g l}^{-1}$

of the line in figure 6 corresponds to the wetting enthalpies

$$\begin{aligned} H_{L,A} &= 18.8 \text{ J/g}_{\text{Aerosil}} \\ &\cong 16.1 \text{ kJ/mole}_{\text{CHCl}_3} \\ &\cong 20.4 \text{ kJ/mole}_{\text{adsorption sites (NEP)}} \\ &\cong 17.8 \text{ kJ/mole}_{\text{adsorption sites (OVP, PVP)}} \end{aligned}$$

Binding enthalpies

The integral adsorption enthalpy $\Delta H(\theta)$ released during the adsorption process of the polymer consists of the enthalpy contributions originating from the formation of surface-polymer contacts as well as from the releases of the solid-solvent and polymer-solvent contacts and an additional contribution of the interaction

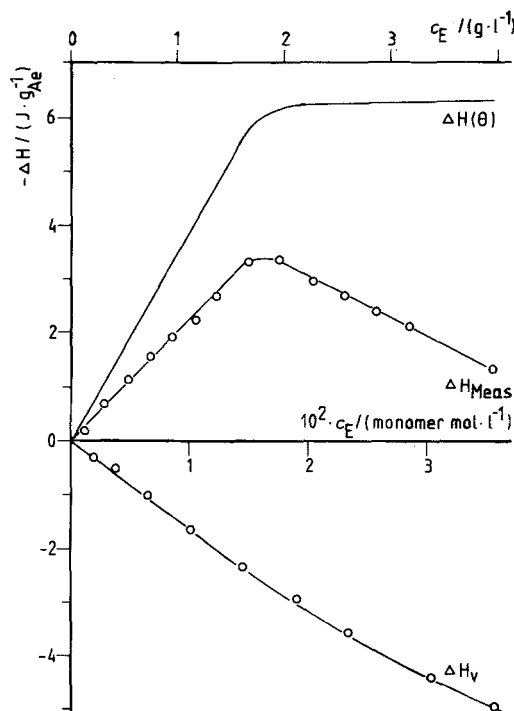


Fig. 4. Measured enthalpy, ΔH_{Meas} dilution enthalpy, ΔH_v , and integral adsorption enthalpy, $\Delta H(\theta)$, as function of the polymer concentration, c_E ; system: PVP, CHCl_3 , Aerosil 200, $c_s = 10 \text{ g l}^{-1}$

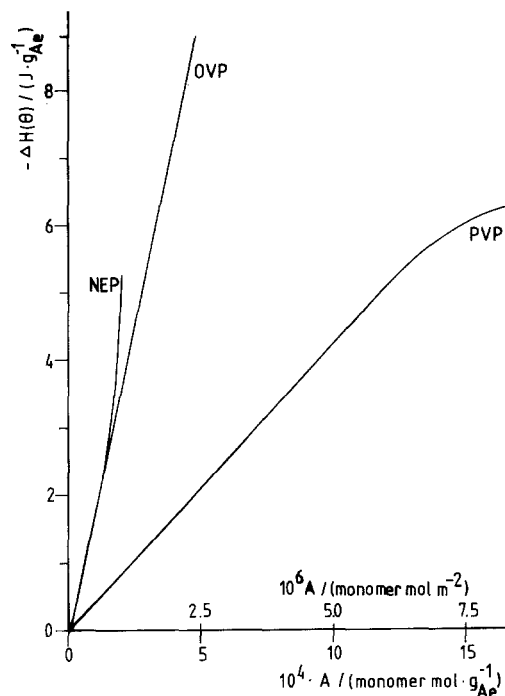


Fig. 5. Integral adsorption enthalpies, $\Delta H(\theta)$, as function of the amount adsorbed, A ; systems: adsorptives, CHCl_3 , Aerosil 200 evacuated at 300 C

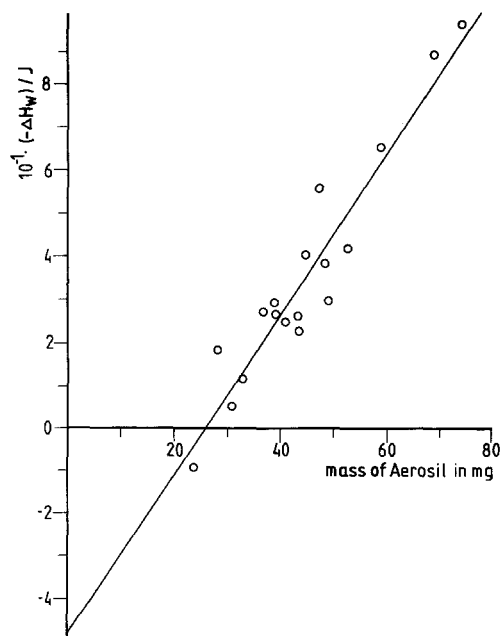


Fig. 6. Measured enthalpy, ΔH_w , produced by the immersion of Aerosil 200 (evacuated at 300 °C) in CHCl_3 as function of the mass of the sample

enthalpy of the polymer molecules in the adsorbed layer with respect to the solution [7]:

$$-\Delta H(\theta) = -n \Delta H_{P,A} + n \Delta H_{L,A} + n \Delta H_{P,L} + \Delta H_{P,P} \quad (2)$$

$\Delta H_{P,A}$ Net binding enthalpy per mole adsorbed polymer segments

$\Delta H_{L,A}$ Solvent-adsorbent interaction enthalpy per mole adsorption sites of the surface

$\Delta H_{P,L}$ Solvent-polymer interaction enthalpy per mole adsorbed segments

$\Delta H_{P,P}$ Interaction enthalpy between adsorbed segments (Flory-Huggins contribution)

n Number of moles of the adsorption sites occupied by polymer segments.

The surface area occupied by one polymer segment is denoted adsorption site and can be determined from calculations using the method of Emmet and Brunauer [16]. Neglecting the last two terms $\Delta H_{P,L}$ and $\Delta H_{P,P}$ with the assumption that they are small compared with the other contributions in equation (2) [6, 7, 17] the binding enthalpy, $\Delta H_{P,A}$, can be determined using the calorimetric measured integral adsorption enthalpy and the wetting enthalpy of the adsorbent in the solvent, $\Delta H_{L,A}$, according equation (3)

$$\Delta H_{P,A} = \Delta H(\theta)/n + \Delta H_{L,A} \quad (3)$$

Introducing the fraction of adhered polymer segments $p_{\text{COH}} = n/A$ equation (4) results:

$$\Delta H_{P,A} = \Delta H(\theta)/(A p_{\text{COH}}) + \Delta H_{L,A} \quad (4)$$

Comparing the surface areas of monomer molecules and polymer-segments with the area of one solvent molecule demands that during adsorption of one molecule, NEP, or one segment of OVP and PVP 1.27 or 1.11 solvent molecules have to be displaced. This is considered in the value of $\Delta H_{L,A}$. The fraction of adhered segments, p_{COH} , was determined by IR measurements [13].

Discussion of the calorimetric results, comparison with data from literature

In table 1 wetting enthalpies, $\Delta H_{L,A}$, fractions of adhered segments, p_{COH} , adsorption enthalpies, $\Delta H(\theta)/A$ and $\Delta H(\theta)/(A p_{\text{COH}})$, and polymer-adsorbent interaction enthalpies, $\Delta H_{P,A}$, calculated with equation (4) from literature data are opposed to own results. The increase of the value $-\Delta H(\theta)/A$ and

Table 1

Adsorptive	Solvent	$-\Delta H_{L,A}$		$-\frac{\Delta H(\theta)}{A}$		$-\frac{\Delta H(\theta)}{p_{\text{COH}}A}$		$-\Delta H_{P,A}$	Ref.
		$\frac{\text{kJ}}{\text{mol}}$	p_{COH}	$\frac{\text{kJ}}{\text{monmol}}$	$\frac{\text{kJ}}{\text{monmol}}$	RT	$\frac{\text{kJ}}{\text{monmol}}$		
NEP	CHCl ₃	20.4	1	18.5 – 25.6	18.5 – 25.6	7.5 – 10.3	38.9 – 46.0	this work	
OVP	CHCl ₃	17.8	0.85 – 0.6	18.2	21.4 – 30.3	8.6 – 12.2	39.2 – 48.1	this work	
PVP K90	CHCl ₃	17.8	0.46 – 0.38	4.2 – 3.8	9.1 – 10.0	3.7 – 4.0	26.9 – 27.8	this work	
PVP K90	Dioxan	24.8	0.48 – 0.25	0.7 – 0.5	1.46 – 1.96	0.6 – 0.8	26.3 – 26.8	[9,10]	
PVP K90	H ₂ O	26.9	0.2 ^a)	0.94 – 0.45	4.7 – 2.2	1.9 – 0.9	31.6 – 29.2	[9,10]	

^a) p_{COH} -value from references [18,19]

$-\Delta H_{P,A}$ with coverage for NEP/CHCl₃ reflects the result from IR spectrometry [13], where the multiple interaction quotient Q increases greatly with coverage. This means that the effective interaction of the monomer with the interface is dependent on coverage. Q -values nearly independent of coverage are found for OVP and PVP from IR. Despite this result the $\Delta H_{P,A}$ values of OVP increase with coverage caused by the decrease of the p_{COH} -values with coverage. For PVP $\Delta H_{P,A}$ is nearly constant with coverage supporting the nearly constant Q -values. The reason for the discrepancy with OVP could be referred to the different contributions of desorbed solvent with coverage ($\Delta H_{L,A}$).

For NEP a wetting enthalpy of 36.8 kJ/mole_{NEP} was determined by Cohen Stuart [9,10]. With equation (4) the adsorption enthalpy of NEP on Aerosil from CHCl₃ leads to interaction enthalpies $\Delta H_{P,A}$ of 38.9 to 46.0 kJ/mole_{NEP}. The agreement of the binding enthalpies resulting from different measurements is satisfying and confirms the accuracy of the foundations used in the calculations. With the "displacer" technique, using adsorptives competing with the adsorbed segments, a segmental free adsorption enthalpy of $\kappa_s = -4$ RT was determined for PVP adsorbed from H₂O and dioxan [11,12]. In comparison an enthalpy value $-\Delta H(\theta)/(p_{\text{COH}}A) = 3.7$ RT was measured for small coverages. The small difference can be attributed to the entropic contribution of the free adsorption enthalpy.

The values $\Delta H(\theta)/p_{\text{COH}}A$ of 0.6 RT and 1.9 RT for the adsorption of PVP from dioxan and H₂O calculated from literature differ distinctly from the cited free

enthalpy values. From this difference an important contribution of the entropy can be concluded. The binding enthalpies $\Delta H_{P,A}$ of 26.3 – 26.8 kJ/mole from dioxan and 31.6 – 29.2 kJ/mole from H₂O calculated using values from Cohen Stuart [9,10] agree satisfactorily with our $\Delta H_{P,A}$ values of 26.9 – 27.8 kJ/mole for the adsorption of PVP from CHCl₃.

Fractions of adhered segments p_{cal} and p'_{cal} for PVP

The oligomeric OVP with high p_{COH} -values, indicating a very flat conformation especially for low coverage, has nearly the same binding enthalpy $\Delta H_{P,A}$ as the monomeric NEP. This justifies in a first approximation the assumption of equivalent interaction enthalpies of polymer segment-adsorbent and of monomer NEP-adsorbent (eq. (7)). The lower $\Delta H_{P,A}$ values of PVP have to be attributed to an additional enthalpy contribution of the displacement of additional solvent molecules by segments not specifically bound on the surface to the magnitude $\Delta H_{L,A}$. This will be discussed later in more detail.

The fraction of adhered segments p_{cal} can be calculated according to the derivation in equations (5) to (8):

$$\Delta H_{P,A} = \left(\frac{\Delta H(\theta)}{A p_{\text{cal}}} \right) p + \Delta H_{L,A,P} \quad (5)$$

$$\Delta H_{M,A} = (\Delta H(\theta)/A)_M + \Delta H_{L,A,M} \quad (6)$$

$$\Delta H_{P,A} = \Delta H_{M,A} \quad (7)$$

$$p_{\text{cal}} = \frac{\Delta H(\theta)/A_P}{(\Delta H(\theta)/A)_M + \Delta H_{L,A,M} - \Delta H_{L,A,P}} \quad (8)$$

Index:

M = monomer

P = polymer

L = solvent

$\Delta H_{L,A,M}$; $\Delta H_{L,A,P}$ = solvent-adsorbent interaction enthalpy per mole adsorption sites of the monomer and of the polymer segments respectively.

The measured values of the specific adsorption enthalpy given in table 1 result in a p_{cal} -value of 0.20 for PVP with equation (8) for the amount adsorbed ($A = 0.75 \cdot 10^{-6} \text{ monmol m}^{-2}$). The corresponding value measured by IR spectrometry amounts to $p_{\text{COH}} = 0.46$. In IR spectrometry, only actual existing hydrogen bonds between the polymer and the adsorbent surface were measured. Therefore the p_{COH} -value obtained represents the lowest limit of the fraction of the polymer segments situated on or in the neighbourhood of the adsorbing surface. The quantities $\Delta H_{L,A,P}$ and $\Delta H_{L,A,M}$ in equation (8) are related to the desorption process of the polymer and monomer segments and can be calculated from the specific wetting enthalpy and the surface area of one polymer or one monomer segment. Because of the covalent binding of the polymer segments in the chain the adsorbed polymer segments cause neighbouring segments to be near or on the surface without being specifically adsorbed, and additionally displace solvent molecules from the surface. This additional displacement of solvent molecules results in an additional enthalpy contribution which has not been considered in the calculation of p_{cal} according to equation (8). This effect may be the reason for the p_{cal} values being smaller than the p_{COH} values.

Assuming a number of y solvent molecules being desorbed during the adsorption of one polymer segment and of x solvent molecules during the adsorption of one monomer molecule, equations (9) and (10) can be formulated:

$$\left(\frac{\Delta H(\theta)}{A p_{\text{COH}}} \right)_P + y \Delta H_{L,A} = \Delta H(\theta)/A_M + x \Delta H_{L,A} \quad (9)$$

$$y - x = \frac{\left(\frac{\Delta H(\theta)}{A} \right)_M - \left(\frac{\Delta H(\theta)}{A p_{\text{COH}}} \right)_P}{\Delta H_{L,A}} \quad (10)$$

With the values in table 1 from equation (10) a value of $(y - x) = 0.59$ is obtained for small coverage. Due to this argumentation during the adsorption of one polymer segment, 0.59 solvent molecules are displaced in excess to the number of solvent molecules displaced during the adsorption of one monomer molecule NEP. The number of the displaced solvent molecules is a measure of the number of segments in the trains, not all having specific interactions with the surface groups.

A fraction of adhered segments, p'_{cal} , can be calculated from equation (11) considering the additional displacement of solvent molecules by polymer segments in comparison to monomer molecules and taking into account the surface areas of the polymer segments and of the monomer molecules.

$$p'_{\text{cal}} = \frac{a_{m,M}/a_{m,L} + (y - x)}{a_{m,P}/a_{m,L}} p_{\text{COH}} \quad (11)$$

With the surface areas for NEP ($a_{m,M}$), PVP ($a_{m,P}$), CHCl_3 ($a_{m,L}$) and the p_{COH} value from IR spectrometry one obtains $p'_{\text{cal}} = 0.77$. The p'_{cal} value 0.77 is between the values $p_{\text{COH}} = 0.46$ from IR spectrometry and those from ESR and NMR spectrometry (0.9 and 0.8 respectively) [9, 10, 18]. Because of low mobility by the ESR method segments are recorded up to a distance of 3 to 5 bond lengths from the fixed segments at the surface [18, 20, 21]. Nearly the same arguments are valid for the NMR method [9, 10].

In the model presented for calculating p'_{cal} , segments taken into consideration are about the diameter of one solvent molecule or about 2 bond lengths from the surface.

In the calorimetrically measured adsorption enthalpy the enthalpy of displacement of these solvent molecules is included. Therefore the p'_{cal} value from the calorimetry has to be between the p value of the IR spectrometry only regarding segments on the surface with specific interaction, and the values from ESR and NMR spectrometry also measuring segments non-specifically adsorbed in the neighbourhood.

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