

# A comparative study of the kinetics and energetics of oligomer desorption from graphite

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## Abstract

The desorption kinetics of polyethyleneglycols (PEGs) of varying chain length,  $N$ , have been studied on the surface of graphite. The chain length dependence of the  $\Delta E_{\text{des}}^{\ddagger}$  has been measured for PEGs and compared with those of  $n$ -alkanes and polyethyleneglycol dimethylethers (PEG-DMEs) adsorbed on graphite. The short PEGs have higher  $\Delta E_{\text{des}}^{\ddagger}$  than PEG-DMEs of comparable length. More importantly, in the short chain regime ( $N < 30$ ) the  $\Delta E_{\text{des}}^{\ddagger}$  of the PEGs are linear in chain length while the  $\Delta E_{\text{des}}^{\ddagger}$  of the  $n$ -alkanes and PEG-DMEs are non-linear in chain length. For long chain lengths ( $N > 30$ ) the  $\Delta E_{\text{des}}^{\ddagger}$  of the PEGs become non-linear and approach those of the PEG-DMEs. The differences between the short chain PEGs and the  $n$ -alkanes and PEG-DMEs are attributable to the hydroxyl endgroups of the PEGs.

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## 1. Introduction

The properties of polymers at a surface or interface are of considerable interest from both a practical and theoretical point of view because of their fundamental importance in numerous technologies including the stabilization of colloidal suspensions, adhesion, and tribology. Adsorption and desorption are also of relevance to the behavior of polymeric lubricants used to protect the surfaces of magnetic storage disks and to the dynamics of the detachment of long chain molecules from catalyst surfaces. As a result the statics and dynamics of adsorbed polymers have been the focus of intense research efforts in recent years [1]. In particular, there has been an emphasis on understanding the kinetics of adsorption and desorption of polymer chains as these processes lead to the formation of an equilibrated adsorbed layer.

The desorption kinetics of small molecules from surfaces are measured and studied routinely using temperature programmed desorption (TPD) spectroscopy. Desorption of small molecules from surfaces is usually considered in terms

of a fairly simple potential energy surface with a single reaction coordinate that describes the motion of the adsorbate from its adsorbed state into the gas phase. The critical parameter that describes the desorption kinetics is the desorption barrier,  $\Delta E_{\text{des}}^{\ddagger}$ , which in transition state theory is the difference between the zero-point energies of the adsorbed species and the transition state to desorption. For desorption of small molecules it is often sufficient to think of the surface normal as the reaction coordinate for desorption. Although the adsorbate–surface interaction potential has many degrees of freedom in addition to the reaction coordinate for desorption, for a small polyatomic adsorbate one generally thinks of these as contributing to the desorption rate constant only through the partition functions for the adsorbed species and the transition state to desorption. For desorption of a linear oligomer, such a description of the system would tend to predict that  $\Delta E_{\text{des}}^{\ddagger}$  should be linear in the chain length. The goal of this work has been to test this assumption by measuring  $\Delta E_{\text{des}}^{\ddagger}$  as a function of chain length for a set of polyethylene glycols (PEGs).

There have been several previous studies which have investigated the effects of chain length on the desorption kinetics of short chain alcohols and alkanes adsorbed

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on various surfaces. Zhang and Gellman used temperature programmed desorption (TPD) to study the reversible adsorption/desorption of a series of straight-chain alcohols ( $\text{CH}_3(\text{CH}_2)_{N-1}\text{OH}$ ,  $N=1-5$ ) on the  $\text{Ag}(110)$  surface and concluded that the  $\Delta E_{\text{des}}^\ddagger(N)$  increased incrementally by  $4.6 \pm 0.4$  kJ/mol per methylene group in the hydrocarbon chain [2]. Millot et al. investigated the desorption of  $n$ -alkanes ( $N=4-8$ ) from silicalite crystals using TPD and found that the  $\Delta E_{\text{des}}^\ddagger(N)$  also scaled linearly with chain length but in increments of 13.5 kJ/mol per methylene unit [3]. The desorption of  $n$ -alkanes ( $N=6-12$ ) from the  $\text{Au}(111)$  surface was studied by Wetterer et al. using helium atom reflectivity [4]. Their study indicated that the  $\Delta E_{\text{des}}^\ddagger(N)$  increased incrementally by  $6.2 \pm 0.2$  kJ/mol per methylene unit. In these and other such studies the range of alkyl chain lengths has been limited to  $N \leq 12$  [5].

Our previous studies of oligomer desorption have used  $n$ -alkanes ( $\text{C}_N\text{H}_{2N+2}$ ,  $N=5-60$ ) [6–8] and polyethyleneglycol dimethylethers (PEG-DMEs,  $\text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{OCH}_3$ ,  $n=1-22$ ) [9,10] adsorbed on graphite. These have shown conclusively that the values of  $\Delta E_{\text{des}}^\ddagger$  measured using temperature programmed desorption (TPD) are non-linear in the chain length and indicate that the desorption process cannot be thought of in the same simple terms as used to describe small molecule desorption. In those studies the empirically observed scaling of the  $\Delta E_{\text{des}}^\ddagger$  with chain length was  $\Delta E_{\text{des}}^\ddagger \approx a + b\sqrt{N}$ . The origin of the non-linearity is the conformational entropy of the chains as they desorb from the surface. One can imagine that an adsorbed oligomer passes through many possible, energetically equivalent configurations on the surface as its structure evolves towards any of the many possible and energetically equivalent transition states to desorption. In essence, there is a multiplicity of energetically equivalent pathways or reaction coordinates along which desorption might occur. This multiplicity of reaction trajectories has been shown to have a significant impact on the desorption kinetics [7,8,10].

We have proposed a model for the desorption mechanism and for the energy and entropy of the conformational states of the  $n$ -alkanes and PEG-DME oligomers adsorbed on graphite [7,8,10]. The model inherently accounts for the multitude of energetically equivalent trajectories, that an adsorbed oligomer might follow leading to desorption. When combined with transition state theory the model can be used to predict the chain length dependence of the measured  $\Delta E_{\text{des}}^\ddagger$  and accurately explains the observed non-linear dependence on chain length for both the  $n$ -alkanes and PEG-DME oligomers. The fits to the data by the models were extremely accurate in both cases and suggest that a common mechanism can be used to describe the detachment processes of alkane and PEG-DME oligomers from surfaces.

In this work, we report the results of studies of the desorption kinetics of long chain polyethyleneglycol oligomers from the surface of graphite. The goal has been to extend the previous work on  $n$ -alkanes and PEG-DME oligomers

by exploring the possible effect on oligomer desorption of functional endgroups such as hydroxyl groups. Desorption rates were measured for a set of monodispersed PEGs ( $\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$ ,  $n=1-20$ ) adsorbed on graphite at coverages ranging from  $<0.1$  monolayers to many multilayers. The range of chain lengths explored in this work is similar to that previously used in our studies of the  $n$ -alkanes [6–8] and the PEG-DMEs [9,10]. In all cases the desorption of the PEGs can be adequately characterized by a first-order rate constant and a  $\Delta E_{\text{des}}^\ddagger$  that is roughly independent of coverage. TPD studies conducted at varying heating rates for initial PEG coverages of  $\sim 1$  monolayer have been used to measure their  $\Delta E_{\text{des}}^\ddagger$  and pre-exponential factors,  $\nu$ , independently. For the PEGs, the  $\Delta E_{\text{des}}^\ddagger$  scale linearly with chain length up to  $N=28$  atoms but non-linearly thereafter. This result is in direct contrast to the results for both the  $n$ -alkanes and PEG-DMEs, whose  $\Delta E_{\text{des}}^\ddagger$  are distinctly *non-linear* over the full range of chain lengths ( $N=5-60$ ). The differences must be attributable to the interactions between hydroxyl endgroups of the PEGs.

## 2. Experimental

All experiments were conducted in a stainless steel ultrahigh vacuum (UHV) chamber with a base pressure of  $10^{-9}$  Torr achieved through use of an ion-pump and titanium sublimation pump. TPD experiments were performed using an ABB Extrel Merlin quadrupole mass spectrometer (QMS). This instrument has a mass range of 1–500 amu and is capable of simultaneously monitoring up to five masses as a function of time during a TPD experiment. In addition, the chamber was equipped with a high molecular weight doser used to expose the surface to compounds with very low vapor pressure.

The substrate used was a 12 mm  $\times$  12 mm  $\times$  2 mm piece of highly oriented pyrolytic graphite (HOPG). Prior to mounting, the sample was cleaved in air to expose the basal plane. The graphite was then mounted on a square piece of tantalum foil  $\sim 0.25$  mm thick using electrically conductive silver epoxy purchased from the Aremco Co. Two tantalum wires were spotwelded to the rear of the tantalum foil and mounted to the end of a manipulator capable of  $x$ ,  $y$ , and  $z$  translation and  $360^\circ$  rotation. Once mounted the graphite could be cooled to  $\sim 120$  K through mechanical contact with a liquid nitrogen reservoir at the end of the manipulator. In addition, the graphite substrate could be heated resistively at a constant rate using a computer to provide proportional-derivative temperature control. The temperature of the tantalum foil was measured using a chromel–alumel thermocouple spot-welded to its rear face. The temperature of the graphite sample was assumed to be that of its tantalum foil mount.

Monodisperse PEGs ( $\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$ ) with  $n=1-2$  were purchased in purities of  $>98.0\%$  from Aldrich Chemicals. Several PEGs with  $n=3-6$  were purchased from Fluka Chemicals in purities of  $>97\%$ . Three relatively monodis-

perse PEGs ( $n \approx 9, 13, 20$ ) each having polydispersities  $< 1.10$  were also purchased from Fluka Chemicals. Although the PEG samples were all nearly monodisperse, each species with  $n \geq 3$  required extensive outgassing prior to use to remove low molecular weight precursors used in their synthesis. This procedure of outgassing or purification consisted of heating the PEG samples in a glass vial under vacuum for  $\sim 12$  h at temperatures ranging from  $45^\circ\text{C}$  for  $\text{H}(\text{OCH}_2\text{CH}_2)_3\text{OH}$  to  $150^\circ\text{C}$  for  $\text{H}(\text{OCH}_2\text{CH}_2)_{20}\text{OH}$ . The purities of the compounds were further verified by measuring the heats of vaporization directly from multilayer desorption peaks observed in their TPD spectra and comparing these measurements with values reported in the literature.

Prior to each set of TPD experiments conducted with a given PEG, the graphite sample was heated in vacuum to  $\sim 1200$  K to induce the desorption of any adsorbed contaminants. Surface cleanliness of the graphite sample has been assumed based on observations made in previous studies [11,12]. In addition, desorption spectra were highly reproducible indicating that no contamination of the surface occurred due to adsorbate decomposition. The desorption peaks for submonolayer coverages of heptane ( $\text{C}_7\text{H}_{16}$ ) were used to assess the reproducibility of the spectra. During a normal TPD experiment using heptane, the peak desorption temperature was consistently found to be  $211$  K and the width of the desorption peak was  $< 7$  K.

The PEGs were introduced into the vacuum chamber using a high molecular weight doser consisting of a heated glass vial mounted at the end of a  $50$  cm long by  $2$  cm diameter dosing tube [7]. During dosing the end of the collimating tube was positioned directly in front of the graphite sample. Deposition of the PEGs with  $n \leq 6$  was performed with the bulk phase maintained at room temperature in the glass vial. Deposition of the bulk PEGs with  $n = 9, 13,$  and  $20$  was performed by heating their bulk phases to  $60^\circ\text{C}$ ,  $80^\circ\text{C}$ , and  $100^\circ\text{C}$ , respectively. No decomposition of the PEGs is expected at the outgassing or deposition temperatures chosen [13].

TPD studies were performed by cooling the graphite sample in UHV to  $\sim 120$  K and exposing its surface to vapor of the PEGs. Following adsorption of the PEGs on the graphite surface, the substrate was positioned approximately  $2$  cm from an aperture leading to the QMS and heated at a constant rate to the temperatures necessary to induce the desorption of all adsorbed species. During heating, the QMS was used to monitor the desorption rate of the adsorbed PEGs and any decomposition products, if present. In all cases, adsorption of the PEGs was both molecular and reversible with no indication of decomposition during heating and desorption.

### 3. Results

The rate of a first-order desorption process from a surface is expressed as

$$r = -\frac{d\theta}{dt} = k_{\text{des}}\theta = \nu \exp\left(\frac{-\Delta E_{\text{des}}^\ddagger}{RT}\right)\theta \quad (1)$$

where  $r$  is the desorption rate,  $\theta$  the fractional surface coverage of the adsorbed species,  $t$  the time,  $k_{\text{des}}$  the desorption rate constant,  $\nu$  a pre-exponential factor for desorption,  $\Delta E_{\text{des}}^\ddagger$  the measured desorption barrier,  $R$  the universal gas constant, and  $T$  the temperature. The following sections describe the determination of the  $\nu$  and  $\Delta E_{\text{des}}^\ddagger$  for the PEGs in the length range  $\text{HOCH}_2\text{CH}_2\text{OH}$  to  $\text{H}(\text{OCH}_2\text{CH}_2)_{20}\text{OH}$  adsorbed on graphite.

#### 3.1. Evaluation of PEG purity

Prior to any detailed analysis of the kinetics of PEG desorption it is necessary to ascertain that the techniques for introduction of the PEGs into the UHV chamber do allow adsorption of a pure, uncontaminated film on the graphite surface. This has been done by measuring the multilayer desorption energies,  $\Delta E_{\text{des}}^{\text{mult}}$ , and comparing them to published values of the heats of vaporization,  $\Delta H_{\text{vap}}$ . Fig. 1 shows the TPD spectra of  $\text{H}(\text{OCH}_2\text{CH}_2)_3\text{OH}$  for different coverages initially adsorbed on the graphite surface at  $120$  K. The TPD spectra were generated by using the QMS to monitor the signal at  $m/q = 45$  ( $\text{C}_2\text{H}_5\text{O}^+$ ) during heating. Several additional

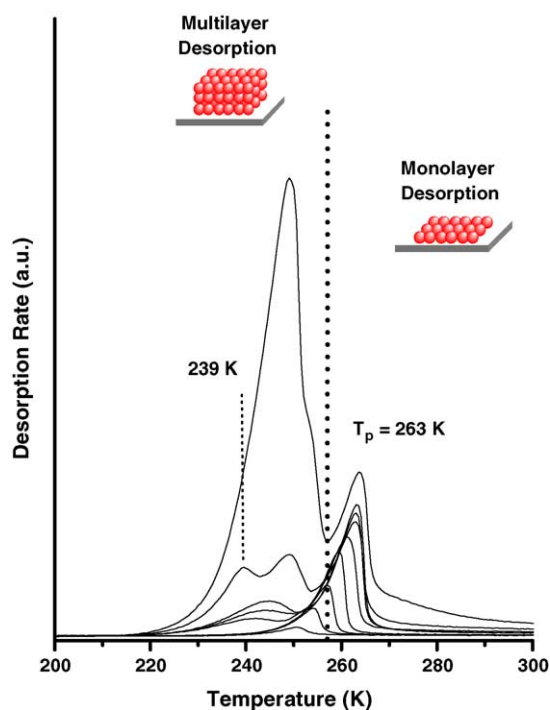


Fig. 1. TPD spectra of  $\text{H}(\text{OCH}_2\text{CH}_2)_3\text{OH}$  adsorbed at various coverages on the graphite surface at  $120$  K. The desorption peak at  $T_p \approx 263$  K is assigned to desorption of the  $\text{H}(\text{OCH}_2\text{CH}_2)_6\text{OH}$  monolayer. The desorption feature at  $T_p \approx 239$  K is assigned to desorption of  $\text{H}(\text{OCH}_2\text{CH}_2)_3\text{OH}$  multilayers. The monolayer desorption temperature is a function of coverage and indicate attractive interactions between adsorbates. The spectra were generated monitoring the signal at  $m/q = 45$  ( $\text{C}_2\text{H}_5\text{O}^+$ ). The heating rate was  $\beta = 2$  K/s.

mass-to-charge ratios were monitored including  $m/q = 59, 73$  and  $89$  to detect desorption of any decomposition products, if present. The desorption signals at these  $m/q$  ratios all occurred at the same temperatures suggesting that they are due to desorption of the same molecule and that there is no decomposition of the  $\text{H}(\text{OCH}_2\text{CH}_2)_3\text{OH}$  on graphite during heating. No decomposition of any of the PEGs studied was observed on the graphite surface during heating.

At the lowest coverage,  $\text{H}(\text{OCH}_2\text{CH}_2)_3\text{OH}$  desorbs over a relatively narrow temperature range ( $\Delta T \sim 7$  K at half-height) and achieves a maximum rate of desorption at  $T_p = 251$  K, as shown in Fig. 1. As the PEG exposure to the surface is increased, the desorption peak increases in intensity and shifts in temperature to  $T_p = 263$  K. This shift and the shape of the peak are distinctive of either a zero-order process or attractive interactions between the adsorbed molecules. Given that the desorption process is molecular it seems most likely that it should be describable as a first-order desorption with attractive interactions between adsorbed species. As the monolayer state approaches saturation, a second desorption feature grows in at  $T_p \sim 239$  K (shifting to  $249$  K at the maximum exposure) which arises from multilayer desorption.

The heat of vaporization,  $\Delta H_{\text{vap}}$ , has been used in this study as a basis for establishing the effectiveness of the techniques used to purify the PEGs. This analysis has been especially important for evaluating the purities of those PEGs that were supplied in polydisperse form. The  $\Delta H_{\text{vap}}$  of the PEGs with  $n \leq 5$  were determined using the relation

$$\frac{d \ln(r)}{d(1/T)} = -\frac{\Delta E_{\text{des}}^{\text{mult}}}{R} \quad (2)$$

to measure the multilayer desorption energy,  $\Delta E_{\text{des}}^{\text{mult}}$ , by using the leading edge of the multilayer desorption peak at highest coverage shown in Fig. 1. The values of  $\Delta E_{\text{des}}^{\text{mult}}$  should be close to the values of  $\Delta H_{\text{vap}}$  of the PEGs. As an example, the data for the desorption of the  $\text{H}(\text{OCH}_2\text{CH}_2)_3\text{OH}$  multilayer are presented in Fig. 2 and reveal that  $\Delta E_{\text{des}}^{\text{mult}} = 80.3 \pm 3.2$  kJ/mol. This is consistent with the value of  $\Delta H_{\text{vap}} = 79.2 \pm 7.9$  kJ/mole for  $\text{H}(\text{OCH}_2\text{CH}_2)_3\text{OH}$  reported by Pedley et al. [14].

The values of  $\Delta E_{\text{des}}^{\text{mult}}$  were determined for the PEGs with  $n \leq 5$ . The  $\Delta E_{\text{des}}^{\text{mult}}$  of the PEGs with  $n \geq 6$  were not determined because the exposures needed to generate multilayer films were too high. Table 1 summarizes the multilayer desorption temperatures observed for the PEGs, the  $\Delta E_{\text{des}}^{\text{mult}}$  determined for the PEGs used in this study and the values of their  $\Delta H_{\text{vap}}$  reported in the literature [14]. The agreement between the  $\Delta E_{\text{des}}^{\text{mult}}$  for the PEGs with  $n \leq 5$  and the values of  $\Delta H_{\text{vap}}$  reported in the literature indicates that the purified PEG samples were free of any low mass contaminants. The correlation between the  $\Delta E_{\text{des}}^{\text{mult}}$  and the  $\Delta H_{\text{vap}}$  for the PEGs with  $n \leq 5$ , suggests that our technique of purification should be sufficient to purify the higher molecular weight PEGs.

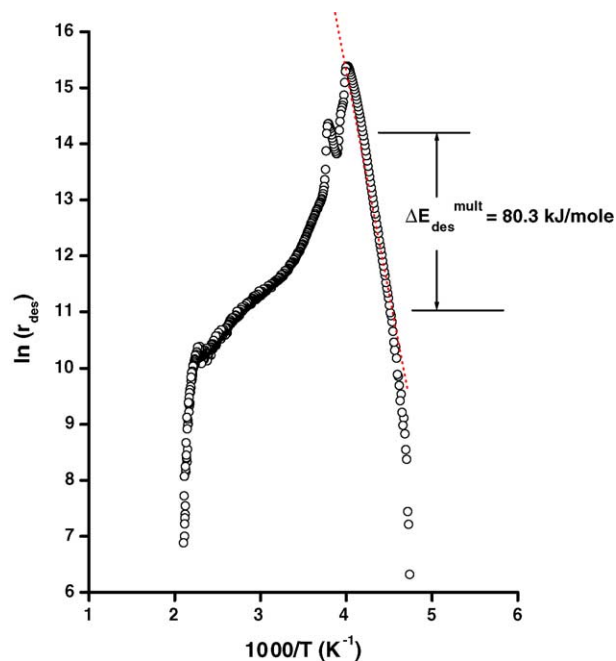


Fig. 2. Arrhenius representation of the TPD spectrum for  $\text{H}(\text{OCH}_2\text{CH}_2)_3\text{OH}$  measured at highest coverage. A line has been fit to the leading edge of the multilayer desorption feature and shows that the  $\Delta E_{\text{des}}^{\text{mult}}$  for  $\text{H}(\text{OCH}_2\text{CH}_2)_3\text{OH}$  is  $80.3 \pm 3.2$  kJ/mol.

The dependence of the desorption spectra on  $\text{H}(\text{OCH}_2\text{CH}_2)_3\text{OH}$  coverage shown previously in Fig. 1 displays characteristics that are common to all of the PEGs studied. In general terms both the monolayer and multilayer peak desorption temperatures,  $T_p$ , increase with the number of ethoxy units,  $n$ , in the backbone of the PEG oligomer. This is shown in more detail in Fig. 3 which illustrates the TPD spectra measured for each of the PEGs for an initial coverage of roughly one monolayer. The  $T_p$  of the monolayer is observed to vary from  $235$  K for  $\text{HOCH}_2\text{CH}_2\text{OH}$  to  $645$  K for  $\text{H}(\text{OCH}_2\text{CH}_2)_{20}\text{OH}$ . The  $T_p$  measured for the PEGs having  $n \leq 6$  were observed to increase by roughly  $10$ – $20$  K upon increasing the coverages from  $<0.1$  monolayer to near monolayer saturation. This coverage dependence of the  $T_p$  disappears for the longer chain PEG oligomers, with  $\text{H}(\text{OCH}_2\text{CH}_2)_{13}\text{OH}$  showing only a  $1$  K increase in the  $T_p$  with increasing coverage.

Table 1  
Multilayer peak desorption temperatures,  $T_p^{\text{mult}}$ , the corresponding desorption energies,  $\Delta E_{\text{des}}^{\text{mult}}$ , and the reported heats of vaporization,  $\Delta H_{\text{vap}}$ , for the PEGs with  $n = 1$ – $5$

Ethylene oxide units ( $n$ )	$T_p^{\text{mult}}$ (K)	Measured $\Delta E_{\text{des}}^{\text{mult}}$ (kJ/mol)	$\Delta H_{\text{vap}}$ (kJ/mol)
1	230	$58.1 \pm 2.1$	$61.9 \pm 6.3^{14}$
2	237	$62.9 \pm 2.8$	$57.3 \pm 5.9^{14}$
3	249	$80.3 \pm 3.2$	$79.2 \pm 7.9^{14}$
4	256	$95.6 \pm 3.8$	$98.7 \pm 10.0^{14}$
5	285	$110.7 \pm 5.5$	$119.8^a$

<sup>a</sup> Estimates based on a linear extrapolation of the published data for PEGs with  $n \leq 4$ .



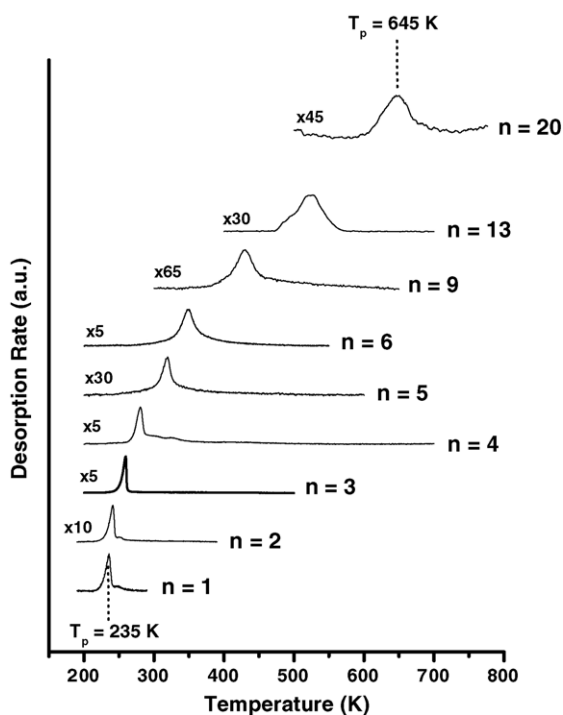


Fig. 3. TPD spectra of the PEGs studied following the adsorption of approximately one monolayer on the graphite surface at 120 K. Both the desorption peak temperature,  $T_p$ , and peak width increase with increasing chain length. All spectra were generated by monitoring the signals at  $m/q=45$  ( $C_2H_5O^+$ ) during heating at  $\beta=2$  K/s.

### 3.2. Measurement of $\Delta E_{des}^\ddagger$ and $\nu$ for PEGs from graphite

The fact that adsorption and desorption of the PEGs on graphite appears to be molecular and reversible suggests that their TPD spectra may be analyzed using a simple Redhead method to give quantitative values of both the  $\Delta E_{des}^\ddagger$  and the pre-exponential factor,  $\nu$  [15]. We have, therefore, measured both  $\nu$  and  $\Delta E_{des}^\ddagger$  independently for the PEGs in an effort to accurately analyze their desorption kinetics from graphite. We present below two methods used to determine both  $\nu$  and  $\Delta E_{des}^\ddagger$  from the TPD spectra. Section 3.2.1 describes the analysis of desorption data using a simple Redhead method, while Section 3.2.2 focuses on obtaining the kinetic parameters through fitting of the TPD spectra to simulated spectra obtained by numerical integration of the desorption rate equation.

#### 3.2.1. Desorption kinetic parameters from Redhead analysis

We have measured both  $\nu$  and  $\Delta E_{des}^\ddagger$  independently for PEG desorption from graphite in an effort to accurately analyze their desorption kinetics. TPD spectra were recorded for the PEGs at various heating rates,  $\beta$ , and initial coverages of approximately one monolayer. The heating rates used in each set of experiments varied from  $\beta=0.2$ –5 K/s. Fig. 4 illustrates the variable heating rate TPD spectra for  $H(OCH_2CH_2)_6OH$

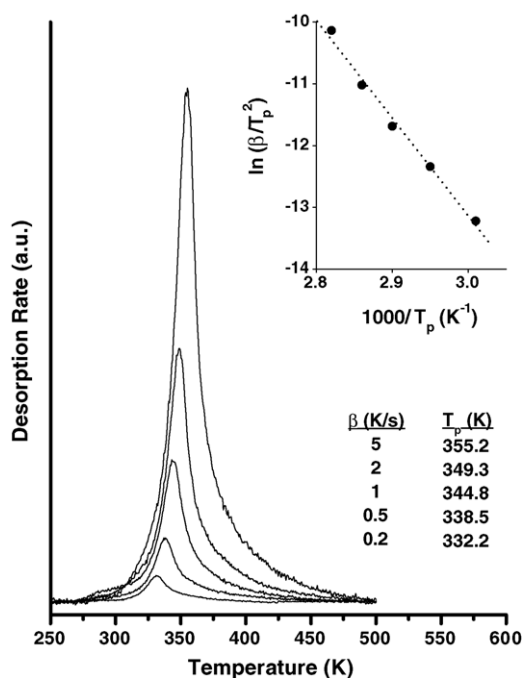


Fig. 4. TPD spectra of  $H(OCH_2CH_2)_6OH$  measured at variable heating rates ( $\beta=0.2$ –5 K/s) for initial coverages of approximately one monolayer. The monolayer desorption temperatures increase with increasing heating rate. The spectra were generated using a mass spectrometer to monitor the signal at  $m/q=45$  ( $C_2H_5O^+$ ) during heating. The inset is a plot of  $\ln(\beta/T_p^2)$  vs.  $1/T_p$  for the desorption of  $H(OCH_2CH_2)_6OH$  from the graphite surface. The slope of the linear fit has been used to estimate the  $\Delta E_{des}^\ddagger$  for  $H(OCH_2CH_2)_6OH$  from graphite.

measured using the QMS to monitor the signal at  $m/q=45$  ( $C_2H_5O^+$ ). The  $H(OCH_2CH_2)_6OH$  monolayer desorbed with a maximum rate at  $T_p=332$  K when the graphite surface was heated at  $\beta=0.2$  K/s. As the heating rate was increased in subsequent experiments, the desorption peaks intensified and shifted to higher temperatures. TPD experiments using a heating rate of 5 K/s induced desorption of the  $H(OCH_2CH_2)_6OH$  monolayer at  $T_p=355$  K.

Analysis of the heating rate dependence of the peak desorption temperature can be used to determine  $\nu$  and  $\Delta E_{des}^\ddagger$  independently. As shown in the inset of Fig. 4, TPD data presented in the form  $\ln(\beta/T_p^2)$  versus  $1/T_p$  yields a straight line whose slope yields a value of  $\Delta E_{des}^\ddagger = 129.0 \pm 5.8$  kJ/mol for  $H(OCH_2CH_2)_6OH$ . Fig. 4 and its inset qualitatively illustrate the desorption behavior of all the PEGs studied using variable heating rate TPD experiments. With the  $\Delta E_{des}^\ddagger$  of the PEGs measured using the variable heating rate method, it is possible to determine the pre-exponential factors for desorption for each PEG. The pre-exponential factors for desorption,  $\nu$ , may be estimated using Redhead's equation [15] for first-order kinetics

$$\nu = \frac{\beta \Delta E_{des}^\ddagger}{RT_p^2} \exp\left(\frac{\Delta E_{des}^\ddagger}{RT_p}\right) \quad (3)$$

Table 2

Desorption barriers,  $\Delta E_{\text{des}}^{\ddagger}$  (kJ/mol), the pre-exponential factors,  $\nu$  ( $\text{s}^{-1}$ ), and the intermolecular interaction parameters,  $\alpha$ , for PEG desorption from graphite determined from Redhead analysis of variable heating rate TPD and by fitting of Eq. (4) to both variable heating rate and variable coverage TPD data.

Ethoxy units ( $n$ )	Redhead analysis of variable heating rate TPD		Fitting to variable heating rate TPD			Fitting to variable coverage TPD	
	$\log_{10}(\nu)$	$\Delta E_{\text{des}}^{\ddagger}$	$\log_{10}(\nu)$	$\Delta E_{\text{des}}^{\ddagger}$	$\alpha$	$\Delta E_{\text{des}}^{\ddagger}$	$\alpha$
1	$15.5 \pm 1.4$	$71.4 \pm 6.2$	16.4	73.3	-0.028	75.0	-0.025
2	$17.3 \pm 0.3$	$82.0 \pm 1.6$	17.6	81.4	-0.028	83.3	-0.032
3	$18.7 \pm 0.9$	$94.3 \pm 4.3$	18.3	92.9	-0.026	90.6	-0.030
4	$18.7 \pm 0.8$	$105.8 \pm 4.5$	18.3	101.9	-0.015	100.9	-0.020
5	$18.4 \pm 0.4$	$116.3 \pm 2.7$	17.8	115.6	-0.015	112.2	-0.023
6	$18.7 \pm 0.9$	$129.0 \pm 5.8$	18.6	134.3	-0.010	132.5	-0.014
9	$19.1 \pm 0.7$	$162.2 \pm 5.8$	20.2	185.9	0.072	182.3	0.081
13	$19.2 \pm 1.3$	$199.6 \pm 13.1$	19.4	204.5	0.081	204.5	0.072
20	ND	$242.7^a$	ND	ND	ND	ND	ND

ND = not determined.

<sup>a</sup> Calculated value based on  $T_p = 645$  K and  $\nu = 10^{18.8} \text{ s}^{-1}$ .

where  $T_p$  depends on the heating rate,  $\beta$ . The pre-exponent for  $\text{H}(\text{OCH}_2\text{CH}_2)_6\text{OH}$  desorption from graphite is  $\nu = 10^{18.7 \pm 0.9} \text{ s}^{-1}$ .

Values of  $\nu$  and  $\Delta E_{\text{des}}^{\ddagger}$  have been measured using Redhead analysis of variable heating rate TPD spectra for the PEGs with  $n = 1$ –13. Columns 2 and 3 of Table 2 list the values of  $\nu$  and  $\Delta E_{\text{des}}^{\ddagger}$  determined from the Redhead analysis for all of the PEGs studied in this work. Note that the value of  $\nu$  has not been determined for  $\text{H}(\text{OCH}_2\text{CH}_2)_{20}\text{OH}$  as the exposures needed to generate a full monolayer were too high. The value of  $\Delta E_{\text{des}}^{\ddagger}$  for  $\text{H}(\text{OCH}_2\text{CH}_2)_{20}\text{OH}$  reported in Table 2 has been calculated using the Redhead equation and a pre-exponential factor of  $\nu = 10^{18.8} \text{ s}^{-1}$  (the average value of  $\nu$  for the PEGs with  $n > 2$ ) and the peak desorption temperature of  $T_p = 645$  K observed in the TPD spectra.

### 3.2.2. Desorption kinetic parameters determined by simulation

In addition to using the Redhead analysis, a second approach was used to obtain values for  $\nu$  and  $\Delta E_{\text{des}}^{\ddagger}$  of the PEGs using both variable coverage and variable heating rate TPD experiments. This approach involved fitting the experimental TPD spectra with simulated spectra generated using the following expression for the desorption rate.

$$r = \nu \exp\left(\frac{-\Delta E_{\text{des}}^{\ddagger} (1 - \alpha\theta)}{RT}\right) \theta \quad (4)$$

The variable  $\alpha$  is a parameter that quantifies the fraction of the  $\Delta E_{\text{des}}^{\ddagger}$  that is attributable to intermolecular interactions. The fitting procedure used  $\nu$ ,  $\Delta E_{\text{des}}^{\ddagger}$ , and  $\alpha$  as free parameters that were allowed to vary to optimize the fit. We will present the results of fitting the TPD spectra obtained with variable heating rates first and then the results of fitting the spectra obtained at different initial coverages.

The set of TPD spectra obtained at varying heating rates for a given PEG oligomer were fit simultaneously to determine the best values of  $\nu$ ,  $\Delta E_{\text{des}}^{\ddagger}$ , and  $\alpha$  for each molecule. The TPD spectra of  $\text{H}(\text{OCH}_2\text{CH}_2)_2\text{OH}$  and the

simulated spectra obtained from Eq. (4) are shown in Fig. 5 for heating rates of  $\beta = 0.2$ –5 K/s and are indicative of the fits obtained for the TPD spectra of the remaining PEG oligomers. The free parameters for  $\text{H}(\text{OCH}_2\text{CH}_2)_2\text{OH}$  assumed final values of  $\nu = 10^{17.6} \text{ s}^{-1}$ ,  $\Delta E_{\text{des}}^{\ddagger} = 81.4$  kJ/mol, and  $\alpha = -0.028$ . The values of  $\nu$ ,  $\Delta E_{\text{des}}^{\ddagger}$ , and  $\alpha$  determined by fitting the variable heating rate TPD spectra for the PEGs are listed in columns 4–6 of Table 2. Comparison with the values for  $\nu$  and  $\Delta E_{\text{des}}^{\ddagger}$  determined through Redhead analysis shows that the two methods yield fairly similar re-

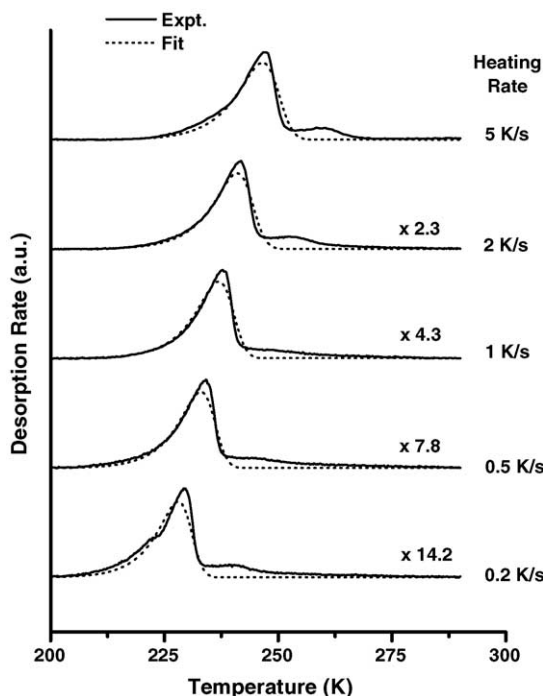


Fig. 5. TPD spectra of  $\text{H}(\text{OCH}_2\text{CH}_2)_2\text{OH}$  measured at variable heating rates (solid line) and the results of a least squares fit to the data using a first-order desorption rate constant (dashed line). The free parameters allowed to vary during the course of the fitting were found to have values of  $\nu = 10^{17.6} \text{ s}^{-1}$ ,  $\Delta E_{\text{des}}^{\ddagger} = 81.4$  kJ/mol, and  $\alpha = -0.028$ .

sults. The fact that the interaction parameters,  $\alpha$ , for the PEGs with chain length  $n \leq 6$  are all negative indicates some weak attractive interactions between the adsorbed PEGs and is consistent with both the peak shapes and the small increases in the peak desorption temperatures as coverage increases.

The TPD spectra recorded at varying coverages and using a constant heating rate of  $\beta = 2$  K/s for each PEG were also fit to the first-order desorption rate equation shown in (4). Fixed heating rate desorption spectra do not decouple  $\Delta E_{\text{des}}^{\ddagger}$  and  $\nu$  so the value of  $\nu$  has been fixed at its value determined through fitting of the variable heating rate spectra. As such, only the  $\Delta E_{\text{des}}^{\ddagger}$ , and  $\alpha$  were allowed to vary as free parameters during fitting. Fig. 6 displays the fits of the simulated spectra to the TPD spectra of  $\text{H}(\text{OCH}_2\text{CH}_2)_2\text{OH}$  for coverages in the range 0.20–1.0 monolayers and qualitatively illustrates the accuracy of the fits for the remaining PEGs. The  $\Delta E_{\text{des}}^{\ddagger}$  and  $\alpha$  for  $\text{H}(\text{OCH}_2\text{CH}_2)_2\text{OH}$  assume values of  $\Delta E_{\text{des}}^{\ddagger} = 83.3$  kJ/mol and  $\alpha = -0.032$ , respectively. Columns 7 and 8 of Table 2 summarize the values of  $\Delta E_{\text{des}}^{\ddagger}$  and  $\alpha$  found for the PEGs by fitting to the variable coverage TPD data. The important point is that  $\Delta E_{\text{des}}^{\ddagger}$  for the PEGs determined through fitting to either the variable heating rate TPD or the variable coverage TPD data are very similar and are very close to the values determined from the Redhead analysis of the TPD spectra obtained with variable heating rates. Given that all three analyses of the PEG desorption spectra yield consistent

results, we will for the purposes of further discussion use the values of  $\Delta E_{\text{des}}^{\ddagger}$  and  $\nu$  listed in columns 2 and 3 of Table 2 that were obtained using the Redhead analysis.

#### 4. Discussion

The goal of the work presented in this paper has been to measure the chain length dependence of the kinetic parameters for PEG desorption in order to make comparisons with the results of previous studies using  $n$ -alkanes and PEG-DMEs. For those molecules we have observed that the measured values of  $\Delta E_{\text{des}}^{\ddagger}$  are non-linear in the chain length,  $N$ . Furthermore, they can be modeled quite effectively as chains of identical, independent segments that attach and detach reversibly to and from the surface in a complex process that ultimately leads to desorption. That model accounts for the energies and entropies of the chains in their various stages of partial detachment and quantitatively reproduces the observed non-linearity in the measured values of  $\Delta E_{\text{des}}^{\ddagger}$ . The difference between the PEGs and the PEG-DMEs (or  $n$ -alkanes) is that they have polar hydroxyl endgroups that can interact through hydrogen bonding with one another. The work presented here probes the influence of such endgroups on the oligomer desorption kinetics and ultimately will serve as the basis for the inclusion of such endgroup effects into our previously developed model for the kinetics of oligomer desorption.

##### 4.1. Chain length dependence of $\nu$

The pre-exponents to PEG desorption listed in column 2 of Table 2 are plotted against the PEG chain length,  $N = 3n + 1$ , in Fig. 7. For the short PEGs the value of  $\nu$  increases with chain length until at a length of  $N = 10$  the values reach a plateau at  $\nu_{\text{avg}} = 10^{18.8 \pm 0.8} \text{ s}^{-1}$ . The difference between this and the results obtained previously is that for the  $n$ -alkanes and PEG-DMEs the pre-exponents do not show any measurable chain length dependence. Their pre-exponents are  $\nu_{\text{avg}} = 10^{19.6 \pm 0.5} \text{ s}^{-1}$  for the  $n$ -alkanes and  $\nu_{\text{avg}} = 10^{18.8 \pm 0.7} \text{ s}^{-1}$  for the PEG-DMEs. These very high values of the desorption pre-exponent for all the long oligomers are quite surprising but have been observed consistently in studies of the desorption of many alkanes and organics from the graphite surface. In fact, the theory developed for understanding the chain length dependence of  $\Delta E_{\text{des}}^{\ddagger}$  does not account adequately for the fact that the pre-exponents for  $n$ -alkane and PEG-DME desorption are independent of chain length [5,8,16]. On the basis of that theory one would expect that the measured desorption pre-exponents should increase for short chains and then decrease for the longer chain oligomers. Although the data for the PEGs does show an increase in the desorption pre-exponents for the short chains, it plateaus at values close to those observed for the long  $n$ -alkanes and PEG-DMEs.

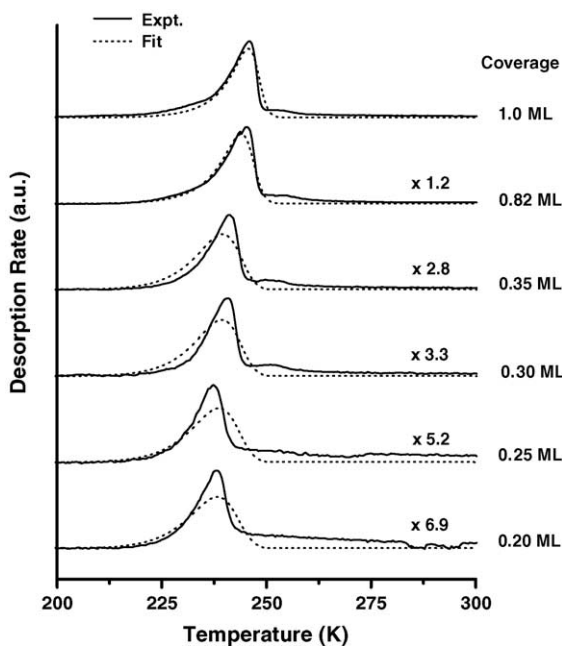


Fig. 6. TPD spectra of  $\text{H}(\text{OCH}_2\text{CH}_2)_2\text{OH}$  measured at variable coverages and a constant heating rate of  $\beta = 2$  K/s (solid line) and the results of a least squares fit to the data using a first-order desorption rate constant (dashed line). The value of  $\nu$  was fixed at  $10^{17.6} \text{ s}^{-1}$  (see Table 2) and the free parameters determined from the fitting were found to be  $\Delta E_{\text{des}}^{\ddagger} = 83.3$  kJ/mol and  $\alpha = 0.032$ .

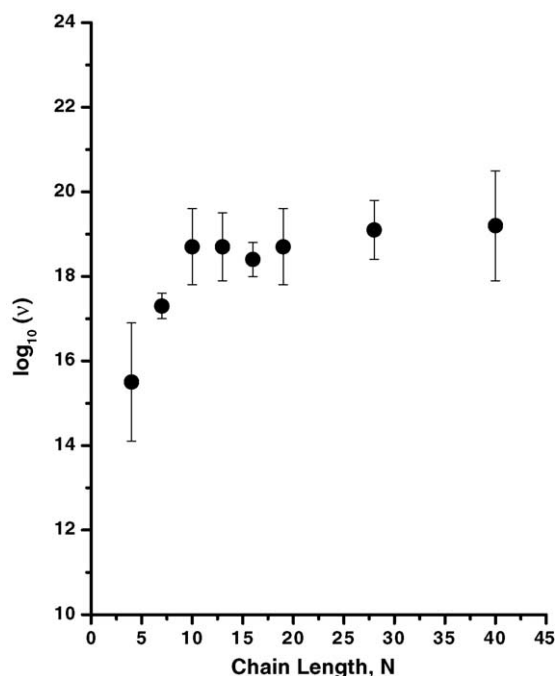


Fig. 7. Pre-exponential factors,  $\nu$ , of the first-order desorption rate constants,  $k_{\text{des}}$ , of the PEGs as a function of chain length. The values of  $\nu$  were calculated using a Redhead analysis of the variable heating rate TPD spectra. The pre-exponential factors for the PEGs with  $n = 1$  and 2 are significantly lower than those of the remaining molecules. The values of  $\nu$  are independent of chain length for the PEGs with  $n > 2$  and have an average value of  $\nu_{\text{avg}} = 10^{18.8 \pm 0.8} \text{ s}^{-1}$ .

#### 4.2. Chain length dependence of $\Delta E_{\text{des}}^{\ddagger}$

The  $\Delta E_{\text{des}}^{\ddagger}$  of the PEGs have been determined from TPD studies using varying heating rates for constant initial PEG coverages of approximately one monolayer and using variable coverage TPD data obtained at a single heating rate. The primary aim of the work has been to determine the effect of chain length on  $\Delta E_{\text{des}}^{\ddagger}$ . For the purposes of this analysis the values of the  $\Delta E_{\text{des}}^{\ddagger}$  reported will be those determined by the Redhead analysis and listed in column 3 of Table 2.

The chain length of the PEGs used in this study are denoted  $N = 3n + 1$  and give the number of C and O atoms in the chain. The chain lengths explored in this work range from  $N = 4$  ( $\text{HOCH}_2\text{CH}_2\text{OH}$ ) to  $N = 61$  ( $\text{H}(\text{OCH}_2\text{CH}_2)_{20}\text{OH}$ ). This representation of the data for the PEGs allows a comparison of the chain length dependence of  $\Delta E_{\text{des}}^{\ddagger}$  for the PEGs with those of the PEG-DMEs ( $N = 6\text{--}69$ ) [9,10] investigated over similar ranges of chain lengths.

The chain length dependence of the  $\Delta E_{\text{des}}^{\ddagger}$  measured for the PEGs on graphite is significantly different from that observed for the  $n$ -alkanes and the PEG-DMEs. Fig. 8 illustrates the  $\Delta E_{\text{des}}^{\ddagger}$  of the PEGs (solid circles) as a function of the chain length,  $N$ . For comparison purposes the solid line shows the empirical fit to the observed values of  $\Delta E_{\text{des}}^{\ddagger}$  of the PEG-DMEs. Whereas the  $\Delta E_{\text{des}}^{\ddagger}$  of the PEG-DMEs (and the  $n$ -alkanes) are non-linear in chain length over the entire

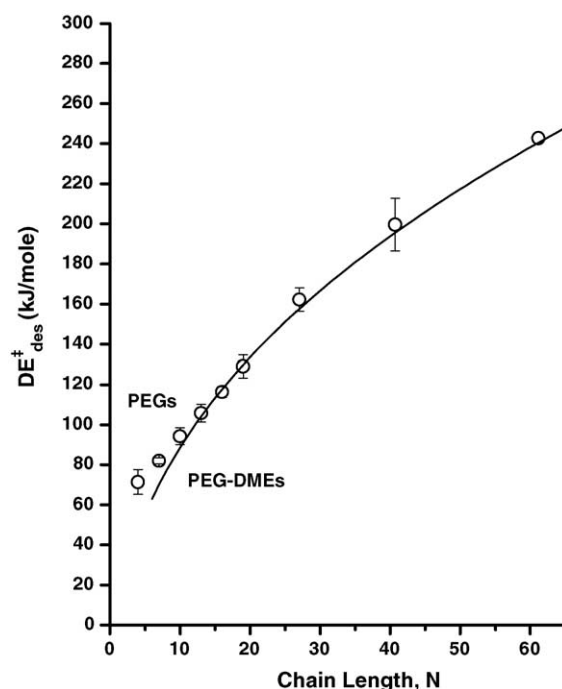


Fig. 8. Desorption barriers,  $\Delta E_{\text{des}}^{\ddagger}$ , of the PEGs from graphite as a function of chain length. The solid line is the empirical curve representing the values of the  $\Delta E_{\text{des}}^{\ddagger}$  found for the PEG-DMEs on graphite [7,8]. The  $\Delta E_{\text{des}}^{\ddagger}$  are linear in chain length for the PEGs with chain lengths lower than  $N \approx 30$  and are higher than the  $\Delta E_{\text{des}}^{\ddagger}$  for the corresponding PEG-DMEs. For longer chain lengths the values of  $\Delta E_{\text{des}}^{\ddagger}$  for the PEGs become non-linear in chain length and approach those of the corresponding PEG-DMEs.

range from  $N = 5\text{--}60$ , it is clear that the  $\Delta E_{\text{des}}^{\ddagger}$  for the PEGs are linear in chain length for  $N \leq 28$  but vary non-linearly thereafter. In the short chain length regime the  $\Delta E_{\text{des}}^{\ddagger}$  of the PEGs exceed those of the PEG-DMEs. This is not surprising given the presence of the polar, hydroxyl endgroups on the PEGs. What is somewhat surprising is the fact that the endgroups somehow modify the chain length dependence of the  $\Delta E_{\text{des}}^{\ddagger}$ . As the chain length increases the influence of the endgroups ought to diminish and as illustrated in Fig. 8 the values of  $\Delta E_{\text{des}}^{\ddagger}$  for the PEGs approach those of the PEG-DMEs. Furthermore, once the chain length reaches  $N \approx 30$  the chain length dependence of the  $\Delta E_{\text{des}}^{\ddagger}$  for the PEGs appears to become non-linear and begins to follow the chain length dependence of the PEG-DMEs.

The origin of the non-linear dependence of the  $\Delta E_{\text{des}}^{\ddagger}$  of the  $n$ -alkanes and the PEG-DMEs on graphite is the configurational entropy of the molecules in the adsorbed state. If the segments of an oligomeric chain such as an alkane were all attached to the surface in the adsorbed state, then one would expect the  $\Delta E_{\text{des}}^{\ddagger}$  to scale linearly with chain length. At finite temperatures, however, the segments of the chain are able to attach and detach from the surface independently. As a consequence, the average energy of the molecules in the adsorbed state,  $\langle E_{\text{ad}} \rangle$ , is higher than that of the fully attached chain. As the temperature increases towards the desorption temperature



a greater fraction of the chains are detached from the surface. The net effect is that the measured value of  $\Delta E_{\text{des}}^{\ddagger}$  is reduced and falls below the desorption energy that one would expect to observe for the fully attached chain.

The fact that the  $\Delta E_{\text{des}}^{\ddagger}$  for the PEGs scale linearly for chain lengths up to  $N \approx 30$  suggests that the short PEG oligomers are constrained to lie flat and fully attached to the surface up to the temperatures at which they desorb. Although no detailed model is being proposed at this point, it is possible that intermolecular hydrogen bonding between chain ends serves to constrain the PEGs to lie flat against the surfaces. In order for internal segments to detach from the surface the length of the molecule along the surfaces must decrease, forcing the separation of chain ends and the loss of intermolecular hydrogen bonding between chain ends. Thus there is a large energy barrier to the detachment of the first segment from the surface and the entire chain is constrained to lie parallel to the surface to higher temperatures than are observed for molecules without functional endgroups. If the chains are still constrained to be parallel to the surface at the desorption temperature, then the measured values of  $\Delta E_{\text{des}}^{\ddagger}$  will increase linearly with chain length.

For sufficiently long chains the endgroup effects in the PEGs must diminish and the kinetics of the desorption process must approach those of the PEG-DMEs. The increase in chain length will cause the oligomers to desorb at higher temperatures and thus to remain on the surface to temperatures at which the hydrogen bonding interactions of the hydroxyl groups can be overcome. Furthermore, entropy effects in the longer chains will favor segment detachment from the surface to a greater extent than in the shorter chains and will also help to overcome the interactions between hydroxyl endgroups. Thus for long chains one expects the chain length scaling of the  $\Delta E_{\text{des}}^{\ddagger}$  to approach those of the PEG-DMEs.

## 5. Conclusions

The kinetics of oligomer desorption from the surface of graphite are influenced significantly by the presence of functional endgroups such as the hydroxyl endgroups of PEGs.

For the PEGs, the measured values of  $\Delta E_{\text{des}}^{\ddagger}$  scale linearly with chain length up to values of  $N \approx 30$  and non-linearly thereafter. In contrast, the  $\Delta E_{\text{des}}^{\ddagger}$  of the *n*-alkanes and the PEG-DMEs, which do not have functional endgroups, scale non-linearly with chain length through the range  $N = 5$ –60. We suggest that the effect of the endgroups in the PEGs may be to constrain their chains to lie flat against the surface to higher temperatures than for the PEG-DMEs.

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