

Desorption kinetics of polyether lubricants from surfaces

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Desorption or evaporation is one of the mechanisms for loss of perfluoropolyalkylether (PFPE) lubricants from the surfaces of data storage media. One approach to minimizing PFPE loss to desorption is the use of lubricants with increasing molecular weight or increasing average chain length. In order to understand the effects of chain length on the lubricant evaporation kinetics we have studied the desorption kinetics of monolayer films of oligomeric ethers with varying chain length adsorbed on the surface of graphite. The desorption pre-exponents, ν , and desorption barriers, $\Delta E_{\text{des}}^{\ddagger}$, have been measured for poly(ethylene glycol) dimethyl ethers, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_m\text{CH}_3$, with $m = 1, 2, 3, 4, 8$ and 10 . These are models for the PFPE known as Fomblin Z, which has a structure $\text{CF}_3\text{O}(\text{CF}_2\text{CF}_2\text{O})_x(\text{CF}_2\text{O})_y\text{CF}_3$. The results show that the desorption pre-exponents are independent of chain length and have an average value of $\nu = 10^{18.7 \pm 0.3} \text{ s}^{-1}$. The $\Delta E_{\text{des}}^{\ddagger}$ for the poly(ethylene glycol) dimethyl ethers vary non-linearly with chain length and can be fit with a power law expression of the form $\Delta E_{\text{des}}^{\ddagger} = a + b \cdot N^\gamma$, where N is the total number of atoms in the oligomer backbone ($N = 3m + 3$) and the scaling exponent has a value of $\gamma \approx 1/2$. This non-linear dependence of $\Delta E_{\text{des}}^{\ddagger}$ on chain length has also been observed in recent studies of the desorption kinetics of straight chain alkanes from graphite. A desorption mechanism is described that explains the non-linearity of $\Delta E_{\text{des}}^{\ddagger}$ for the poly(ethylene glycol) dimethyl ethers. The implication for the lifetime of lubricants on data storage media is that the long chain PFPE lubricants desorb more rapidly than one might expect based on simple linear scaling of the $\Delta E_{\text{des}}^{\ddagger}$ of lower molecular weight PFPEs.

KEY WORDS: perfluoropolyalkylether; magnetic data storage; lubricants; desorption; graphite

1. Introduction

Lubrication of the hard disk surfaces used for magnetic data storage is one of the most high-tech and most demanding problems in modern tribology. In hard disk drives data is written to and read from the surface of the disk by a small read-write head that flies over the disk surface at speeds of several meters per second and a height of 200–300 Å. The constant demand for increased data storage density can only be met by continually decreasing the gap between the read-write head and the disk surface. Lubrication and wear protection of the disk surface is critical, since intermittent contacts between the read-write head and the disk surface are unavoidable and would cause catastrophic damage to the magnetic media if it were not protected in some way. Currently, the magnetic media is a thin (~150 Å) film of magnetic material that is sputtered onto the disk surface. It is protected from damage due to contact with the read-write head by an overcoat of amorphous hydrogenated or nitrogenated carbon that is ~50 Å thick. Additional protection is provided by a thin film of perfluoropolyalkylether (PFPE) lubricant that is <20 Å in thickness. The extremely small gap between the read-write head and the magnetic media places enormous constraints on the nature of the carbon overcoat and the lubricant film. These constraints are becoming greater as the demand for higher areal storage densities requires lower and lower fly heights for the read-write head [1–5].

There are many interesting issues associated with the performance and the lifetime of the overcoat and the lubricant used for tribological protection of data storage media. From the perspective of surface chemistry this

is an intriguing problem. The PFPE lubricants are random copolymers or oligomers with a structure of $\text{R}-\text{CF}_2\text{O}(\text{CF}_2\text{CF}_2\text{O})_x(\text{CF}_2\text{O})_y\text{CF}_2-\text{R}$ and molecular weights in the range 2000–8000 amu. These are molecular chains that are 50–200 atoms in length (~50–200 Å) with diameters of ~7 Å. In other words the lubricant film on the disk surface is only about two monolayers thick with the PFPE chains lying roughly parallel to the surface. As a consequence the properties of this lubricant film are directly dictated by the molecular level interactions of the PFPE with the surface of the carbon overcoat. Issues such as lubricant mobility, lubricant desorption, and lubricant rheology that will affect its performance and its lifetime must be understood at the molecular level. The focus of this paper is an understanding of the kinetics and the mechanism of the desorption of oligomeric lubricants from surfaces. Lubricant is certainly lost to desorption or evaporation under normal operating conditions of a disk drive [6]. One of the obvious approaches to reducing desorption would be the use of lubricants with longer chain lengths or higher molecular weights. One might expect that the kinetic barrier to desorption, $\Delta E_{\text{des}}^{\ddagger}$, might increase linearly with chain length and thereby reduce the desorption rate. Unfortunately, very little is known about the desorption kinetics of such long chain oligomers from surfaces.

This paper describes work that is part of a larger effort to understand the desorption of oligomers from surfaces and, in particular, the effort to quantify the effect of chain length on desorption kinetics. Previous work made use of a set of 21 straight chain alkanes, $\text{H}(\text{CH}_2)_N\text{H}$, with chain lengths in the range $N = 5-60$ carbon atoms and measured both the desorption pre-exponents, ν , and desorption barriers, $\Delta E_{\text{des}}^{\ddagger}$,

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from the surface of graphite [7,8]. The desorption kinetics are well described by a first-order rate equation with a rate constant having a pre-exponent that is independent of chain length and a $\Delta E_{\text{des}}^{\ddagger}$ that varies *non-linearly* with chain length. In fact, the dependence of the $\Delta E_{\text{des}}^{\ddagger}$ on alkane chain length takes the form $\Delta E_{\text{des}}^{\ddagger} = a + b \cdot N^{\gamma}$ with the exponent having a value of $\gamma = 0.50 \pm 0.01$. A model for the desorption mechanism and for the oligomer–surface interactions has been proposed that describes the non-linear dependence of the $\Delta E_{\text{des}}^{\ddagger}$ on chain length. The primary insight that is gained from that model is that the non-linearity in the $\Delta E_{\text{des}}^{\ddagger}$ is due to conformational isomerism of the oligomer as it passes along a complex reaction path from the adsorbed species to the desorbed state.

The amorphous carbon overcoat used to protect disk surfaces contains hydrogen or nitrogen and has a complex surface that is composed of both sp^2 and sp^3 carbon atoms in various degrees of partial oxidation. Its surface is certainly quite heterogeneous. Although graphite is not a perfect model for the overcoat surfaces it does have the virtue of being homogeneous and is composed purely of sp^2 hybridized carbon atoms that, under vacuum, can be kept perfectly free of oxidation. This paper reports the initial results of measurements of the desorption kinetics of a set of poly(ethylene glycol) dimethyl ethers, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_m\text{CH}_3$, with $m = 1, 2, 3, 4, 8$ and 10 , adsorbed on the surface of graphite. The homogeneity of the surface is necessary for the measurements reported in this paper. The poly(ethylene glycol) dimethyl ethers, which will henceforth be referred to as PEG-DMEs, are models for the PFPE lubricant known as Fomblin Z which has the structure $\text{CF}_3\text{O}(\text{CF}_2\text{CF}_2\text{O})_x(\text{CF}_2\text{O})_y\text{CF}_3$. The differences, of course, are that the PEG-DMEs are hydrogenated rather than fluorinated and they are homopolymers rather than random copolymers. The measurements that are reported in this paper show that the desorption of the PEG-DMEs from the graphite surface can be described as a first-order process with a rate constant having a pre-exponent that is independent of chain length. Much more importantly the measured values of $\Delta E_{\text{des}}^{\ddagger}$ vary non-linearly with chain length. Furthermore, this behavior is very similar to that observed for the alkanes on graphite and can be described empirically by the expression $\Delta E_{\text{des}}^{\ddagger} = a + b \cdot N^{\gamma}$ with $\gamma = 0.48 \pm 0.02$. The implication is that the behavior observed for alkane desorption from the surface of graphite is quite generic and that the model previously proposed for the mechanism of alkane desorption can be used to understand the desorption kinetics of other oligomeric species including the PFPE lubricants used on data storage media.

2. Experimental

All experiments were conducted in a stainless steel ultra-high vacuum (UHV) chamber with a base pressure of 10^{-9} Torr achieved through use of an ion-pump and titanium sublimation pump. The apparatus and procedures used

have been described in detail elsewhere [7]. The graphite sample was mounted on a UHV manipulator that allowed cooling to 100 K and heating to 1000 K. The surface of the graphite was prepared simply by peeling off the top layers in air immediately prior to insertion into the UHV chamber and heating to 1000 K once under vacuum. All indications are that this procedure gives a surface that is clean and yields highly reproducible desorption spectra of either the alkanes or the PEG-DMEs. The PEG-DMEs were all obtained from the Aldrich Chemical Co. Prior to use they were extensively purified in order to remove all low molecular weight contaminants. Exposure of the surface to the low molecular weight PEG-DMEs was achieved by use of a leak valve while the higher molecular weight species were introduced into the vacuum chamber through the use of an evaporative doser specifically designed for use with these very low vapor pressure compounds. Following adsorption of the PEG-DMEs on the graphite surface at 100 K, the substrate was positioned approximately 2 cm from the aperture to an ABB Extrel Merlin quadrupole mass spectrometer and heated at a constant rate to the temperatures necessary to induce the desorption of all adsorbed species. In order to examine the effects of coverage on the desorption kinetics, thermally programmed desorption (TPD) spectra were obtained at PEG-DME coverages that varied from <0.1 monolayer (ML) to >2 monolayers using a constant heating rate (β) of 2 K/s. Furthermore, in order to obtain accurate kinetic parameters for the desorption process the TPD spectra were obtained at PEG-DME coverages of ~ 1 ML using constant heating rates that covered the range $\beta = 0.2\text{--}5$ K/s. During heating, the mass spectrometer was used to monitor the desorption rate of the adsorbed species and any decomposition products, if present. In all cases, desorption of the PEG-DMEs was both molecular and reversible with no indication of decomposition.

3. Results

The first experiments in our study of the desorption kinetics of the PEG-DMEs have determined the order of the desorption process. This is most easily achieved by examining the dependence of the desorption kinetics on coverage and is done by obtaining TPD spectra at varying initial coverages of the PEG-DMEs on the graphite surface using a constant heating rate of $\beta = 2$ K/s. Figure 1 shows the TPD spectra obtained for tetra(ethylene glycol) dimethyl ether, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_3$, adsorbed on the graphite surface at coverages ranging from 0.1 to 2 ML. At low coverages there is a single desorption peak at 295 K that increases in intensity with increasing coverage and shifts to a temperature of 300 K. The peak intensity saturates at high coverage and this peak has been assigned to the desorption of the monolayer directly adsorbed to the graphite surface. As the coverage is increased past the point at which the monolayer desorption feature saturates, a second desorption feature appears

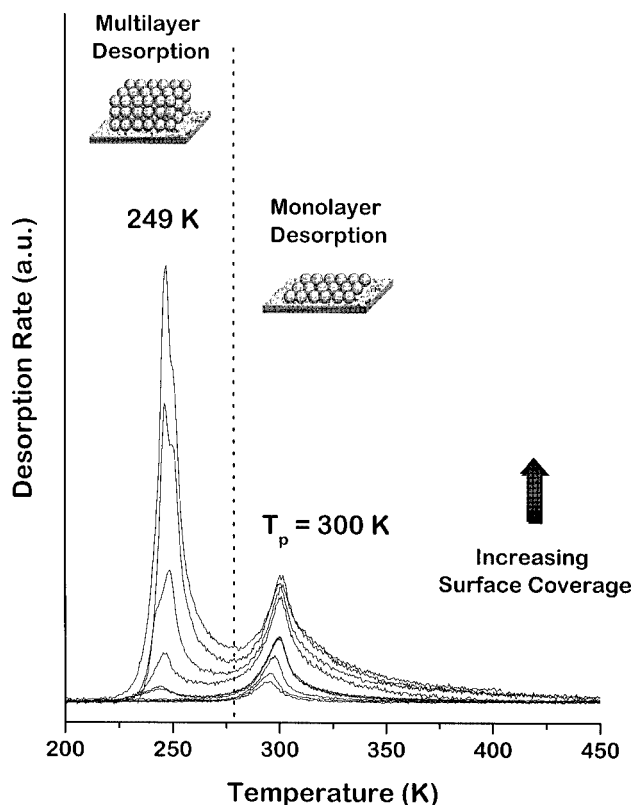


Figure 1. TPD spectra of $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_3$ desorption from the surface of graphite. The monolayer desorption feature is observed at $T_p = 300$ K and is independent of coverage, indicating that the desorption process is first order. The peak observed at 249 K is due to multilayer desorption. The spectra were obtained by monitoring the mass spectrometer signal at $m/q = 45$ and using a heating rate of 2 K/s.

at 249 K. This feature grows in intensity without apparent bound and has desorption kinetics that appear to be zero-order in coverage, in that the leading edges of these peaks overlap one another. This feature is assigned to multilayer desorption from the surface.

TPD spectra have been obtained for desorption of PEG-DMEs with $m = 1, 2, 3, 4, 8$ and 10 from the graphite surface during heating at a constant rate of $\beta = 2$ K/s. All spectra give the same qualitative desorption behavior as that illustrated in figure 1. In all cases the peak desorption temperature for the monolayer feature in the TPD spectra is fairly independent of coverage. This behavior is characteristic of a first-order desorption process with a $\Delta E_{\text{des}}^\ddagger$ that is independent of coverage. Previous studies of the desorption of the n -alkanes from the surface of graphite also indicate that desorption is a first-order process with a coverage independent $\Delta E_{\text{des}}^\ddagger$ [7,8]. In addition to being first-order we find that the desorption of the PEG-DMEs from the graphite surface occurs without decomposition.

Given that the desorption of the PEG-DMEs from the graphite surface can be described with a first-order rate constant of the form

$$k = \nu \cdot \exp\left(-\frac{\Delta E_{\text{des}}^\ddagger}{RT}\right)$$

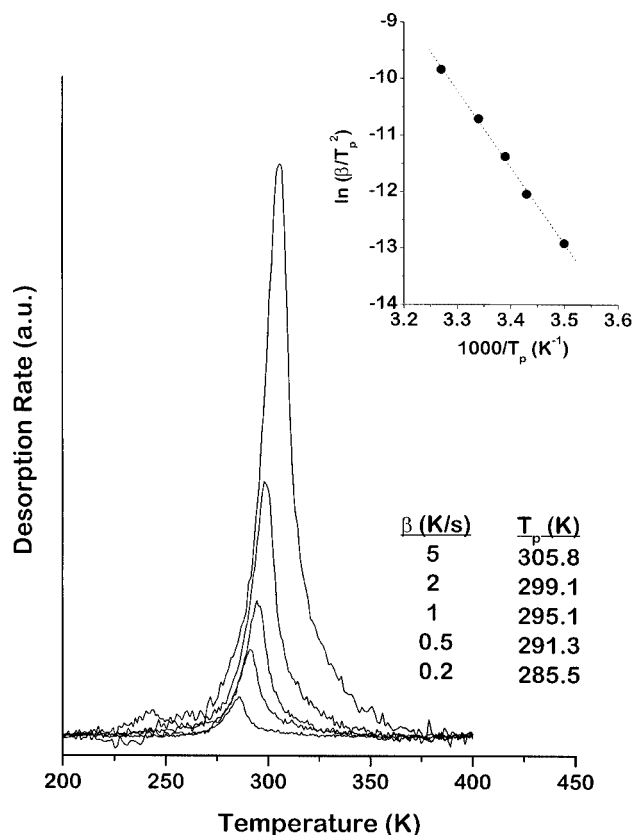


Figure 2. TPD spectra of $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_3$ desorption from the surface of graphite obtained at heating rates in the range $\beta = 0.2$ –5 K/s for initial coverages of ~ 1 ML. The dependence of the peak desorption temperature, T_p , on the heating rate, β , can be used to determine the desorption energy, $\Delta E_{\text{des}}^\ddagger$. The inset shows a plot of $\ln(\beta/T_p^2)$ versus $1/T_p$ which has a slope of $-\Delta E_{\text{des}}^\ddagger/R$.

we have set about measuring the kinetic parameters, ν and $\Delta E_{\text{des}}^\ddagger$, by obtaining TPD spectra at different heating rates in the range $\beta = 0.2$ –5 K/s for initial PEG-DME coverages of ~ 1 ML. Examples are shown in figure 2 for the desorption of tetra(ethylene glycol) dimethyl ether monolayers. The increase in the peak desorption temperature, T_p , with increasing heating rates can be used to determine the $\Delta E_{\text{des}}^\ddagger$ by using the Redhead equation in the form [9]

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{R \cdot \nu}{\Delta E_{\text{des}}^\ddagger}\right) - \frac{\Delta E_{\text{des}}^\ddagger}{RT_p}$$

The inset in figure 2 shows a plot of $\ln(\beta/T_p^2)$ versus $1/T_p$ which yields a value of $\Delta E_{\text{des}}^\ddagger = 112 \pm 3$ kJ/mol. With this number in hand the desorption pre-exponent has been determined to be $\nu = 10^{19.0 \pm 0.5} \text{ s}^{-1}$. Similar analyses of the TPD spectra for the other PEG-DMEs used in this study have determined the values of ν and $\Delta E_{\text{des}}^\ddagger$ as a function of chain length.

The principal goal of this work has been to determine the chain length dependence of the desorption kinetics of the PEG-DMEs from the graphite surface. The desorption pre-exponents have been found for all six PEG-DMEs and are independent of chain length, with an average value of $\nu =$

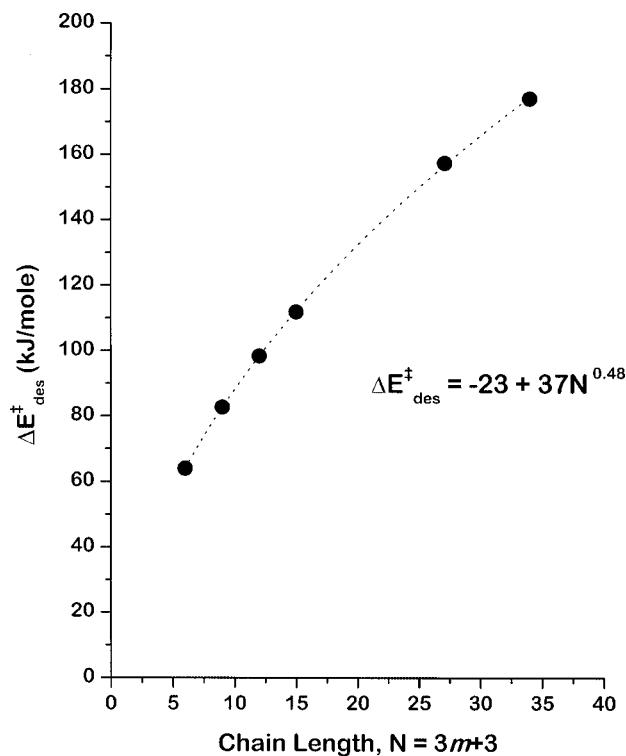


Figure 3. The measured values of the desorption energies of the PEG-DMEs adsorbed on graphite as a function of the oligomer chain length, $N = 3m + 3$. The results reveal the clear non-linear dependence of the $\Delta E_{\text{des}}^{\ddagger}$ on chain length. This non-linear behavior can be fit with the empirical expression $\Delta E_{\text{des}}^{\ddagger} = a + b \cdot N^{\gamma}$, where $a = -23 \pm 6$ kJ/mol, $b = 37 \pm 4$ and $\gamma = 0.48 \pm 0.02$.

$10^{18.7 \pm 0.3} \text{ s}^{-1}$. The independence of ν on chain length was also observed for the desorption of alkanes from the surface of graphite [8]. For the alkanes the desorption pre-exponent was also quite high having a value of $\nu = 10^{19.6 \pm 0.5} \text{ s}^{-1}$. The more interesting result of our measurements is the relationship between the $\Delta E_{\text{des}}^{\ddagger}$ and the chain length which is plotted in figure 3. The $\Delta E_{\text{des}}^{\ddagger}$ are clearly non-linear in the chain length. Although the range of chain lengths used for the alkanes on graphite is somewhat greater than for the PEG-DMEs, the same general behavior and functional dependence of $\Delta E_{\text{des}}^{\ddagger}$ on chain length is observed for both. What is most interesting is that the values of $\Delta E_{\text{des}}^{\ddagger}$ can be fit very well with the empirical expression $\Delta E_{\text{des}}^{\ddagger} = a + b \cdot N^{\gamma}$, where $N = 3m + 3$ for the PEG-DME compounds. In the case of the PEG-DMEs the empirical fit to this functional form gives values of $a = -23 \pm 6$ kJ/mol, $b = 37 \pm 4$ and $\gamma = 0.48 \pm 0.02$. These are quite similar to the values obtained for the alkanes on graphite [7,8]. In particular the scaling exponent for the alkanes had a value of $\gamma = 0.50 \pm 0.01$.

4. Discussion

The similarity in the chain length dependence of the $\Delta E_{\text{des}}^{\ddagger}$ for both the alkanes and the PEG-DMEs indicates that the same basic mechanism and physics is controlling

their desorption kinetics. The fact that the scaling exponent for the $\Delta E_{\text{des}}^{\ddagger}$ has a value of $\gamma \approx 1/2$ for both the alkanes and the PEG-DMEs reveals a common behavior that is particularly intriguing but not fully understood at this point. We have, however, proposed a discrete model for the desorption of the n -alkanes from graphite which quantitatively reproduces the observed dependence of the $\Delta E_{\text{des}}^{\ddagger}$ on chain length and apparently is equally applicable to the desorption of the PEG-DMEs [7,8].

The desorption mechanism previously proposed for the n -alkanes considers a chain of segments interacting with the surface. The segments are equated with the C–C bonds, so an alkane with N carbon atoms has, in this case, $N - 1$ segments. At any given temperature the segments of the chain are attaching and detaching reversibly from the surface so that the surface is covered with chains having various numbers of detached segments, n , ranging from $n = 0$ (fully adsorbed) to $n = N - 2$ (all-but-one segment detached). The relative coverages of the species with varying numbers of detached segments are given by θ_n and are related to one another by equilibrium constants. The irreversible step in the desorption process is the detachment of the last attached segment of those species with all-but-one segment already detached (i.e., $n = N - 2$). Analysis of this desorption mechanism reveals that the $\Delta E_{\text{des}}^{\ddagger}$ measured at a given temperature is given by the difference in energy of the transition state to desorption, $E_{\text{des}}^{\ddagger}$, and the energy of the adsorbed species with minimum free energy, E_{min} ,

$$\Delta E_{\text{des}}^{\ddagger} = E_{\text{des}}^{\ddagger} - E_{\text{min}}.$$

It is important to realize that the species with minimum free energy does not necessarily have all segments attached to the surface. Although this configuration may minimize the energy, E , of the adsorbed chain, the configurational entropy gained by allowing segments to detach from the surface dictates that at temperatures above $T = 0$ K the species with minimum free energy, $A_{\text{min}} = E_{\text{min}} - T S_{\text{min}}$, will have some segments detached from the surface. This is the origin of the non-linear dependence of the $\Delta E_{\text{des}}^{\ddagger}$ on chain length.

In order to equate the model for oligomer desorption from surfaces with the measured values of $\Delta E_{\text{des}}^{\ddagger}$ one needs a model for the interactions of the oligomer with the surface which will yield the free energy, A_n^{N-1} , of a species having $N - 1$ bonds or segments, n of which are detached from the surface. This can then be used to determine the value of n which minimizes the free energy. The simplest formulation of this model sets the energy of such a species as

$$E_n^{N-1} = n \cdot E^{\text{bs}}.$$

In other words the energy is linear in the number of detached segments and the species with all segments attached to the surface is the reference state with $E_0^{N-1} = 0$. The quantity E^{bs} represents the bond-surface interaction energy and is an unknown parameter that is determined by fitting the experimental data for $\Delta E_{\text{des}}^{\ddagger}(N)$ to the predictions of our model. The statistics of chain conformations that can be adopted by

the adsorbed oligomers with some fraction of their segments detached from the surface gives the partition function,

$$q_n^{N-1} = \frac{(N-1)!}{n!(N-n-1)!} \cdot 3^n.$$

The first term is simply the number of ways in which n of $N-1$ segments or bonds can be detached from the surface. The second term represents the number of configurations that can be taken by the n detached bonds each of which can adopt *trans*, *+gauche*, or *-gauche* configurations. The partition function is related to the entropy through the Boltzmann equation,

$$S_n^{N-1} = k \cdot \ln(q_n^{N-1})$$

and gives the free energy of each conformation,

$$A_n^{N-1} = E_n^{N-1} - T \cdot S_n^{N-1}.$$

The number of detached segments which minimizes the free energy at the desorption temperature, T , then determines the $\Delta E_{\text{des}}^\ddagger$ predicted by the model. This model has given an extremely good fit of the $\Delta E_{\text{des}}^\ddagger$ for the alkanes on the graphite surface [7]. Given that these show the same general behavior as the desorption energies for the PEG-DMEs studied in this work, it is quite likely that the same model describes their desorption quite accurately.

The results of this work have important implications for understanding of the desorption kinetics of PFPEs from the surfaces of hard disk data storage media. It is quite apparent from the work presented here that the $\Delta E_{\text{des}}^\ddagger$ of such long chain oligomers do not scale linearly with chain length. Although it is certainly the case that increasing the chain length increases the $\Delta E_{\text{des}}^\ddagger$ and thus decreases the rate of desorption, the $\Delta E_{\text{des}}^\ddagger$ do not increase in the simple way that one might expect. This means that the rates of desorption for high molecular weight PFPEs are probably much higher than one might expect on the basis of linear scaling of the $\Delta E_{\text{des}}^\ddagger$ measured for lower molecular weight PFPEs. Another aspect of data storage tribology in which these ideas may well be important is the diffusion of PFPEs. Diffusion of the PFPEs is necessary in order to refill areas of the disk surface that have been depleted of lubricant due to contact with the head flying over the media surface. Diffusion is also a strong function of chain length and it is quite likely

that the mechanism for diffusion is influenced by chain conformations that serve to partially detach the molecule from the disk surface [10,11]. The work that is presented here reports the first attempts to quantify this behavior in hydrocarbon ethers that serve as analogs for the PFPE lubricants used on data storage media.

5. Conclusions

The $\Delta E_{\text{des}}^\ddagger$ of oligomeric ethers as measured by thermal desorption methods have been shown to increase non-linearly with chain length. This behavior has been shown to be very similar to that observed for the n -alkanes on graphite. The source of the non-linearity is the conformational entropy of the oligomers as they are heated on the surface. This can be accounted for by considering the statistics for detachment of oligomer segments from the surface and the conformations that can be adopted by the detached bonds.

Acknowledgments

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References

- [1] A.J. Gellman, *Curr. Opin. Colloid Interface Sci.* 3 (1998) 368.
- [2] C.M. Mate, *Picking the Best Lubricant for Contact Recording*, Data Storage (July 1997) pp. 45–48.
- [3] H.M. Kryder, *Mater. Res. Soc. Bull.* 21 (1996) 17.
- [4] C.M. Mate and A.M. Homola, *Micro/Nanotribology and its Applications*, ed. B. Bhushan (Kluwer, 1997) pp. 647–661.
- [5] D.A. Thompson, *J. Magn. Soc. Jap.* 21 (1997) 9.
- [6] G.W. Tyndall and R.J. Waltman, *J. Phys. Chem. B* 104 (2000) 7085.
- [7] K.R. Paserba and A.J. Gellman, *J. Chem. Phys.*, submitted.
- [8] K.R. Paserba and A.J. Gellman, *Phys. Rev. Lett.* 86 (2001) 4338.
- [9] P.A. Redhead, *Vacuum* 203–211 (1962).
- [10] B.G. Min, J.W. Cjoi, H.R. Brown, D.Y. Yoon, T.M. O'Connor and T.E. Karis, *Tribol. Lett.* 1 (1995) 225.
- [11] X. Ma, J. Gui, L. Smoliar, K. Grannen, B. Marchon, M.S. Jhon and C.L. Bauer, *J. Chem. Phys.* 110 (1999) 3129.