Adsorption and Mixing Behavior of Ethers and Alkanes at the Solid/Liquid Interface

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The behavior of binary mixtures of linear symmetrical ethers and alkanes adsorbed to a graphite surface from the bulk liquid mixtures is described on the basis of differential scanning calorimetry (DSC) data. Both the ethers and the alkanes are found to form solid monolayers when adsorbed from the liquid. In addition, the monolayer mixing behavior is addressed. The results indicate that there is good, essentially ideal, mixing in the monolayers for ethers and alkanes of the same overall chain length, where the chain length is equal to the total number of carbon and oxygen atoms in the molecule. However, a difference in chain length of more than one atom results in a variation of mixing behavior from nonideal mixing (for long pairs) to phase separation (for short pairs) on the graphite surface. Hence, we conclude that it is the relative chain lengths that control mixing behavior. The results are quantified using a regular solution model with a correction for preferential adsorption. The phase behavior of the mixed monolayers is also compared to the behavior of the bulk. Interestingly, we observe mixtures where the bulk and monolayer behavior are quite different, for example, phase separation in the bulk but essentially ideal mixing in the monolayer for mixtures of ethers and alkanes with the same chain lengths. At present, we attribute this mixing in the monolayer to dilution of the unfavorable ether oxygen−ether oxygen lone pair interactions by the coadsorbed alkanes. In addition, we find evidence for the preferential adsorption of the alkane over the ether. For example, heptane is preferentially adsorbed over dibutyl ether even though it contains two fewer atoms in the molecular chain. This contrasts with the preferential adsorption of alcohols over alkanes reported previously (Messe, L.; Perdigon, A.; Clarke, S. M.; Inaba, A.; Arnold, T. *Langmuir* **2005,** *21,* 5085−5093).

Introduction

The adsorption of molecules from liquids and solutions to solid surfaces is central to many academic and industrial processes such as lubrication, catalysis, and detergency. Industrial applications typically utilize multicomponent mixtures because the mixtures are cheaper than the pure components or because the mixtures exhibit superior performance relative to the pure components alone. Understanding the mixing behavior of compounds at the solid/liquid interface is thus of great importance.

There are several chemical groups that are particularly important in commercial surface active materials such as anionic surfactants like SDS (sodium dodecyl sulfate), cationics like CTAB (cetyl trimethylammonium bromide), and nonionics like polyoxyethylene alkyl ethers, which consist of an alkyl chain and many ether groups (ethylene oxide, EO) of the form C_nEO_m. In this work, we focus on the two key chemical groups that make up these nonionics, alkyl chains and ether groups.

The adsorption and mixing behavior of nonionic surfactants has attracted significant research attention recently, and there are several researchers who have investigated the interactions between nonionics and other surfactants, both in the bulk and at the solid−liquid interface (for example, see refs 2−5). The extent of interaction of the surfactants is conveniently expressed in terms of an "interaction" parameter from regular solution theory, which represents the difference in interaction energies between the two components relative to the average interaction

energies of the molecules with themselves.[6] Thus, the interaction parameter is related to the excess enthalpy of mixing, providing a measure of the departure of the mixture's behavior from ideality.[1]

Previously, we have presented data on the behavior of solid monolayers adsorbed from mixtures of two linear alkanes,[7,8] two linear alcohols,[9−11] and two linear carboxylic acids[12] to a graphite surface. Binary mixtures of linear alkanes with linear alcohols have also been reported.[1] In brief, all of the pure materials and their binary mixtures have been found to form solid monolayers adsorbed from the liquids and mixtures. For mixtures between homologues, it is found that the longer member is adsorbed preferentially. Alkane/alcohol heteromixtures exhibit more complicated behavior with a shorter alcohol adsorbing preferentially over a longer alkane.[1] The mixing behavior of homologues appears to be mainly governed by the plane groups of the pure monolayer crystal structures and the relative sizes of the two molecules. Alkane/alcohol heteromixtures have large unfavorable enthalpies of mixing independent of molecular size that probably arise from the disruption of the hydrogen bonding between alcohols by coadsorbed alkanes.[1] The alkane/alcohol heteromixtures show poor mixing behavior and are all observed to essentially phase-separate in the monolayer.

Scanning tunneling microscopy (STM) studies have demonstrated the formation of solid monolayers of the long-chain symmetrical ethers hexadecyl ether ($CH_3(CH_2)_{15}O(CH_2)_{15}CH_3$ referred to as $C_{16}OC_{16}$),[13−16] dioctadecyl ether ($C_{18}OC_{18}$),[17] and docosyl ether ($C_{22}OC_{22}$)[14] adsorbed from saturated solutions in 1-phenyloctane onto graphite. The ethers adsorb in their all-

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trans configurations aligned with one of the three equivalent directions of the graphite lattice, similar to the alkanes.[13,15] However, the molecules adopt a "tilted" lamellar structure where the molecules are arranged parallel to one another at an angle of 60° with respect to the lamellar axis, an offset that is attributed to a reduction of oxygen−oxygen lone pair repulsions.[13] The orientation of the carbon backbone with respect to the graphite surface is not reported. Nishino et al.[18] have suggested a perpendicular orientation for the diethers $CH_3(CH_2)_{15}O(CH_2)_nO$-$(CH_2)_{15}CH_3$ ($C_{16}OC_nOC_{16}$) where $n = 10$ and 11 adsorbed from 1,2,4-trichlorobenzene to graphite on the basis of their STM studies with tips chemically modified with 4-mercaptobenzoic acid.

Adsorbed monolayers of thioethers and coadsorbed monolayers of ethers/thioethers and thioethers/alkanes have also been demonstrated by STM. Interestingly, hexadecyl sulfide ($C_{16}SC_{16}$) forms a lamellar structure on graphite where the parallel thioether molecules are aligned perpendicular to the lamellar axis, similar to the odd alkanes and long-chain even alkanes.[13,14] Further, hexadecyl sulfide and hexadecyl ether are reported to form a mixed monolayer on graphite with perpendicular alignment of the molecules with respect to the lamellar axis.[13] The same structure is also reported in the mixed monolayer of hexadecyl sulfide and the alkane tritriacontane ($C_{33}H_{68}$), where Padowitz and Messmore[13] note that the sulfur atom is similar in size and conformation to the methylene groups in the alkane chain. The tritriacontane was observed to preferentially adsorb over the hexadecyl sulfide; the ratio of thioether to alkane on the surface adsorbed from an equimolar solution of hexadecyl sulfide and tritriacontane ranged from 1:5 to 1:15.[14]

In addition to the tilted structure described above, docosyl ether ($C_{22}OC_{22}$) is reported to form a second phase on graphite of lamellae with molecules perpendicular to the lamellar axis,[14] although the formation of the second phase may have been promoted by the STM scanning. Pure docosyl sulfide ($C_{22}SC_{22}$) is also observed to form a phase with molecules perpendicular to the lamellar axis. Docosyl ether and docosyl sulfide form a mixed monolayer on graphite with molecules that are tilted in the lamellae. Some regions with perpendicular alignment of the molecules with respect to the lamellar axis were also observed during scanning. The docosyl ether appears to be preferentially adsorbed over the docosyl sulfide.

In this paper, we report the formation of solid monolayers by short, linear symmetrical ethers adsorbed onto graphite from their pure liquids as detected by differential scanning calorimetry (DSC). In addition, the mixing behavior of combinations of short-chain linear alkanes and the linear symmetrical ethers in the monolayer is reported. Analysis of our data allows us to extract quantitative parameters characterizing the preferential adsorption and the mixing behavior. The results are discussed in terms of the observed bulk behavior and monolayer structure.

Experimental Methods

Calorimetry. The calorimetry measurements were made on a Perkin-Elmer power-compensated Pyris 1 DSC as described previously.[7,19] The heating rate of 10 °C min^{-1} was found to be a suitable compromise between the increased resolution of slow scanning and the increased sensitivity of fast scanning. DSC is a technique in which the heat transferred to or from a sample relative to a reference is measured as a function of temperature with changes in the heat flow (peaks in the thermogram) corresponding to phase transitions. The dynamic nature of the technique has many repercussions. For a first-order bulk melting transition, the peak maximum in a DSC

thermogram is not a good estimate of the transition temperature. During a first-order phase transition, the sample remains at the transition temperature until the transition is complete, while the DSC increases the temperature of the sample and reference at a fixed rate. Hence, the beginning or "onset" of a transition is identified as a better estimate of the true transition temperature. The onset of a first-order transition is found by extrapolating the leading edge of the peak back to the baseline. For a higher-order transition, which monolayer melting may be, the peak maximum position may be a better estimate of the transition temperature.[7] In addition, given the uncertainty of the extrapolation required to estimate the onset of the rather weak monolayer transitions, the peak maximum is often more reliably established. For the monolayer transitions of particular interest here, the differences between the peak and onset temperatures are typically only 1−1.5 °C. In this work, onset values are reported for the bulk melting transitions, which are always first-order, and peak temperatures are reported for the monolayer melting transitions. The uncertainty in all the reported transition temperatures is approximately 1 °C.

The ethers and alkanes were obtained from Sigma-Aldrich at ≥99% purity (except for dihexyl ether at ≥97% purity) and were used without further purification. The recompressed exfoliated graphite Papyex (Le Carbone Lorraine, France) with a specific surface area of 29.9 m^2 gram^{-1}, as determined by nitrogen adsorption, was used. The graphite was cleaned by degassing under vacuum at 350 °C prior to sample preparation. Samples typically consisted of 15 mg of graphite dosed at room temperature with approximately 40 equivalent monolayers of adsorbate, usually 7−10 mg. The adsorbate consisted of either the pure liquid ether or a mixture of the pure liquid ether and pure liquid alkane. An equivalent monolayer is an estimate of the amount of compound required to cover the graphite surface with a single layer of molecules. The number of equivalent monolayers was estimated from the areas per molecule calculated from the model of Groszek[20] and the specific surface area of the graphite. Here, we assumed that the ether oxygen occupies approximately the same surface area as a methylene group (CH_2). Samples were annealed at elevated temperature at least 20 °C below the flash point or boiling point of the adsorbates (whichever was lower) for 2−3 h to DSC measurement. For samples with flash points below room temperature, the samples were annealed at room temperature overnight.

The mixing and preferential adsorption behavior of the ether and alkane binary mixtures was determined by a quantitative fit to the experimental variation in monolayer melting point with composition as determined from the DSC measurements. We have used the regular solution approach for incomplete mixing in the solid monolayer and preferential adsorption on the surface developed from the models of Everett[21,22] and surfactant system applications,[6] the details of which can be found elsewhere.[1] Briefly, the model has two parameters. The first is an interaction parameter Ω related to the difference in energy between A−B interactions and the mean of the A−A and B−B interactions. $\Omega = 0$ indicates ideal mixing and larger positive values indicate increasingly poor mixing in the monolayer up to $\Omega = 2RT$ for phase separation in the monolayer. A phase diagram with a pronounced minimum in the monolayer melting point variation with composition implies a large value of Ω. The second parameter, K, is the equilibrium coefficient for the exchange of short molecules adsorbed to the surface for long molecules and thus reflects the degree of preferential adsorption of a component. A value of $K = 1$ indicates equal adsorption of the long and short molecules and $K > 1$ indicates preferential adsorption
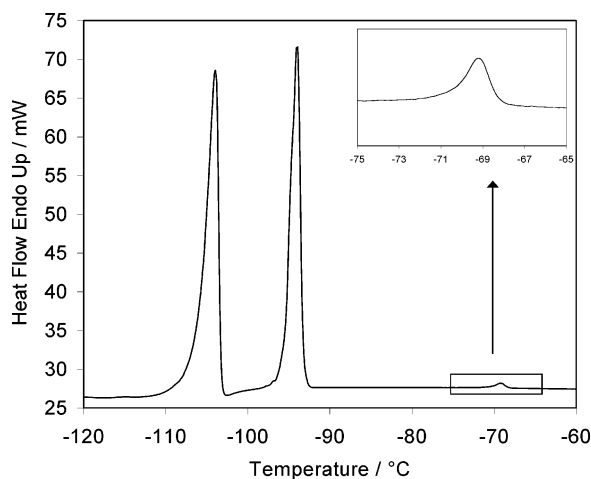
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Figure 1. DSC thermogram of approximately 40 equivalent monolayers of dibutyl ether on graphite. The lowest temperature peak is most likely due to a solid−solid bulk transition in the dibutyl ether, followed by the melting transition of the bulk solid dibutyl ether. The inset is an enlargement of the melting transition of the solid adsorbed monolayer.

of the longer molecule. The position of the minimum on the composition axis is used to determine the value of K. Hence, fitting of the experimental monolayer melting temperature variation with composition is used to determine Ω and K for each pair of mixed molecules.

X-ray Diffraction. Powder X-ray diffraction was used to examine the bulk mixing behavior of the dihexyl ether/dodecane mixtures. The pure materials and the $x_{\text{dihexyl ether}} = 0.49$ mixture were added to a Lindemann glass capillary (0.7-mm internal diameter). X-ray powder diffraction data were collected using Co Kα_1 radiation ($\lambda = 1.79$ Å) on a Stoe Stadi-P diffractometer (Department of Chemistry, University of Cambridge) operating in Debye−Scherrer geometry. A Cryostream device was used to maintain the temperature at 200 K. Diffraction patterns were collected from $2\theta = 3-40$ degrees using a scanning detector.

Results and Discussion

Symmetrical Ethers. Figure 1 shows the DSC thermogram from approximately 40 equivalent monolayers of the linear, symmetrical dibutyl ether (C_4OC_4, DBE) adsorbed on graphite. The large peak at −95.6 °C corresponds to the melting of the pure bulk DBE in good agreement with the literature melting point (−95.4 °C). The much weaker peak above the bulk melting point at −69.1 °C (see inset) is not present in the thermogram of the pure adsorbate nor in that of the bare graphite and is hence attributed to the adsorbed monolayer, as observed for many other materials.[7,12,23,24] Hence, we conclude that DBE does adsorb a solid monolayer from its liquid to the graphite surface. This finding is also supported by STM observations of the adsorption of ordered monolayers of longer ethers and thioethers from 1-phenyloctane solutions.[13−17]

The large peak at −106.1 °C is attributed to a solid−solid phase transition in the bulk adsorbate. Interestingly, this solid−solid transition is only observed in the presence of graphite, indicating that the graphite acts to stabilize the transition. Similar behavior has been reported for adsorbed alkanes with rotator phases appearing for much shorter alkanes in the presence of a graphite substrate than for the pure bulk alkanes.[8]

Similar data for two linear, symmetrical ethers with longer alkyl chains, dipentyl ether (C_5OC_5, DPE) and dihexyl ether (C_6OC_6, DHE), also clearly indicated the formation of solid monolayers on graphite adsorbed from their pure liquids. The

TABLE 1: Temperatures and Enthalpies of the Solid−Solid (S−S) and Melting Transitions (bulk) of the Bulk and Melting Transition of the Monolayer (mono) for Linear Symmetrical Ethers Determined by DSC[a]

ether	$T_{\text{S-S}}$/°C	T_{bulk}/°C	T_{mono}/°C	ΔH_{mono}/kJ mol^{-1}
dibutyl ether	−106.1	−95.6	−69.1	7.1
dipentyl ether		−70.5	−30.4	7.4
dihexyl ether		−42.3	-3.5	11.2

[a] The onset temperature is reported for the bulk solid−solid and melting transitions and the peak temperature is reported for the monolayer melting transitions with an uncertainty of ±1 °C. The experimentally determined enthalpy in J per gram of graphite was converted to kJ per mole of ether using the estimated areas of the molecules from the model of Groszek[20] and the surface area of the graphite. The uncertainty in the enthalpy is ±2 kJ mol^{-1}.
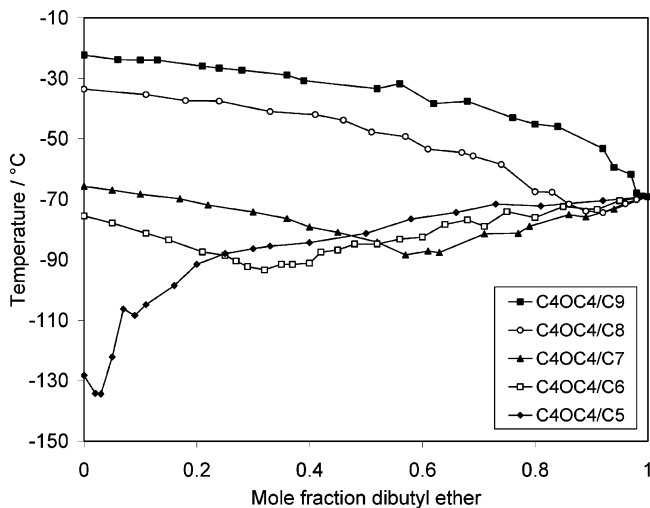

Figure 2. Monolayer melting temperature as a function of bulk mixture composition for binary mixtures of dibutyl ether with nonane, octane, heptane, hexane, and pentane.

bulk melting points and monolayer melting points of the ethers studied here are presented in Table 1.

Dibutyl Ether and Alkane Mixtures. Figure 2 presents the variation in monolayer melting point as a function of the bulk mixture composition for binary mixtures of dibutyl ether (DBE) and the alkanes nonane (C_9), octane (C_8), heptane (C_7), hexane (C_6), and pentane (C_5). The formation of solid monolayers by pure alkanes adsorbed on graphite has been well established by calorimetry,[7,25] STM,[26] incoherent elastic neutron scattering,[7,27] NMR,[28] and X-ray and neutron diffraction.[29−31] The alkane monolayer melting points can be seen at the pure alkane end of these phase diagrams. The continuity of the alkane monolayer transitions with that of the reported DBE monolayer melting point also strongly supports the assignment of the DSC transitions as monolayer melting.

Except for DBE/nonane, the plots in Figure 2 show pronounced minima indicative of nonideal mixing in the monolayer.[32] The minima shift in composition as the alkane chain length is varied, indicating preferential adsorption of one component over the other, will be discussed later. In contrast, the variation in the monolayer melting point for the DBE/nonane combination does not have such a minimum but is rather a smooth curve more typical of good, essentially ideal mixing.

Figure 3 presents representative fits of the regular solution model to the data for (a) DBE/octane, showing poor mixing and for (b) DBE/nonane, showing essentially ideal mixing. Figure 4a presents the experimentally determined Ω values for all of the studied mixtures, normalized by $2RT$, plotted against the relative size ratio $\Delta n/\bar{n}$, the difference in chain lengths of
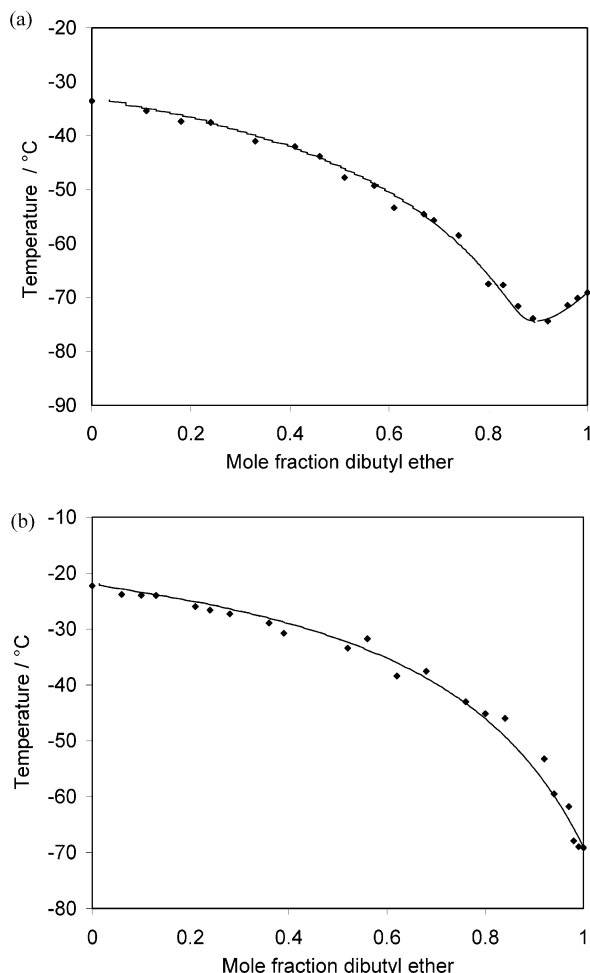
Figure 3. Monolayer phase diagrams for (a) DBE/octane and (b) DBE/nonane on graphite as a function of bulk mixture composition. The diamonds are the experimental points. The solid curves were calculated using the regular solution model described in the text for (a) poor mixing in the monolayer and preferential adsorption of the octane and (b) ideal mixing and preferential adsorption of the nonane.

the ether and alkane divided by the average chain length. The temperature used in normalizing Ω is the temperature of the minimum monolayer melting point on the phase diagram of each binary mixture. This normalization provides a clearer comparison with the condition for phase separation than Ω alone, used in previous work.[1] For the purpose of calculating the relative size ratio, the chain length was defined as the number of carbon and oxygen atoms in the molecule. The interaction parameters of the DBE/alkane mixtures besides DBE/nonane (data points at $\Delta n/\bar{n} > 0.1$) were all greater than zero, indicating that mixing between the DBE and alkanes in the monolayer was endothermic with interactions between like molecules more favorable than "cross" interactions between DBE and the alkanes. The Ω value required to fit the DBE/pentane ($\Delta n/\bar{n} = 0.57$) data was greater than $2RT$, the point at which the monolayer mixture will separate into two phases: one rich in ether and the other rich in alkane. As Ω increases above $2RT$, the composition of the two phases will become richer in each of the pure compounds to the exclusion of the other species.[32]

Figure 4a shows an unexpected variation in Ω with size ratio for the DBE/alkane mixtures. It is clear that the DBE/nonane combination, with a size ratio of zero, has very good mixing and a low value of Ω. However, the value of Ω rises very quickly when the alkane is shortened to octane ($\Delta n/\bar{n} = 0.12$) and remains at a high, essentially constant value with increasing
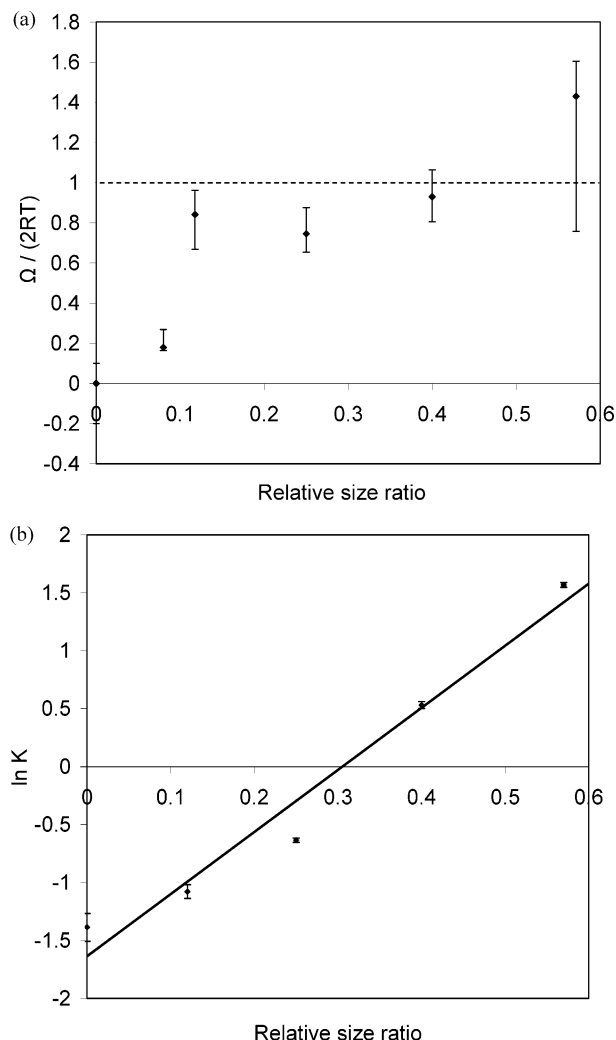

Figure 4. (a) Experimentally determined variation of $\Omega/2RT$ with relative size ratio for the ether/alkane monolayer mixtures. All values are from the DBE/alkane series except for the data point at relative size ratio = 0.08, from the DHE/dodecane system. The dashed line at $\Omega/2RT = 1$ indicates the boundary above which there is extensive phase separation in the monolayer. The error bars reflect the uncertainty in Ω, the range of temperature values in the experimental phase diagrams that could be used to calculate $2RT$, and the likely nonideality of the adsorbed liquid. (b) Experimentally determined variation of ln K with relative size ratio for the dibutyl ether/alkane series from nonane to pentane. ln $K = 0$ indicates the equivalence point of $K = 1$ when both species are equally adsorbed.

relative size ratio (remembering that the much higher DBE/pentane data point only reflects a slightly greater extent of phase separation in the monolayer). This suggests a dominant, unfavorable interaction from mixing an ether with an alkane in the solid monolayer if the alkane is one or more units shorter than the ether. This contrasts with the alkane/alkane mixtures where there is a gradual rise in Ω with relative size mismatch and the alcohol/alkane mixtures where the value of Ω is large even at a relative size ratio of zero and nearly constant across the size ratio range.[1] What is interesting here is that Ω indicates mixing in the monolayer when the ether and alkane are the same length but rises quickly for even a small size mismatch in the DBE and alkane.

Figure 4b illustrates that for nonane, octane, and heptane, K < 1 indicating that the alkanes are preferentially adsorbed and that the exchange of the shorter alkanes for the longer DBE on the graphite surface is not favorable thermodynamically. Only for the much shorter alkanes, hexane and pentane, is $K > 1$

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indicating that for these alkanes the DBE is preferentially adsorbed. The "cross over" point of K, approximately unity, occurs between heptane ($K = 0.53 \pm 0.01$) and hexane ($K = 1.7 \pm 0.05$) at a relative size ratio of 0.31. The variation of increasing ln K values with relative size ratio appears to follow an approximately linear relationship.

The uncertainty in the values of Ω and K, used to determine the error bars in Figure 4a and 4b, depends on the monolayer melting point variation. If there is a pronounced minimum in the data, then both the Ω and K values can be determined with good precision. If the data follows a more smooth variation without a sharp minimum, the precision in Ω and K is less. The uncertainty in $\Omega/2RT$ also reflects the temperature range of the experimental phase diagrams and the likely nonideality of the liquid mixtures (discussed below).

Previous work investigating homomixtures of alkane/alkane and alcohol/alcohol molecules indicates that ln K passes through the origin in a plot of ln K versus relative size ratio and shows a general increase in ln K with increasing size ratio, reflecting that the longer homologue is always preferentially adsorbed to the graphite over the shorter homologue.[1] Heteromixtures of alkanes with alcohols that are the same length or shorter than the alkanes show an approximately linear variation with relative size ratio, but the line does not pass through the origin, instead appearing similar to that seen for DBE/alkanes in Figure 4b.[1] This indicates the stronger adsorption of an alcohol over an alkane (experimentally, an alcohol can adsorb equally as strongly as an alkane that is two methylene groups longer).[1]

Our results suggest that the ether/alkane data is an interesting inversion of the alkane/alcohol case. In the alkane/alcohol system, the oxygen-containing species is more strongly adsorbed relative to the alkane. Here, we have reported evidence that the oxygen-containing ethers are not the preferentially adsorbed species relative to the alkanes. In alcohols, strong hydrogen bonding is expected to favor adsorption, creating an effectively "longer" molecule, although more complex and extended hydrogen-bonding arrangements are likely.

In interpreting these results, the ether oxygens can be expected to have two effects. First, the repulsion between the lone pairs of adjacent molecules will be expected to disfavor ethers being close to one another in a monolayer, and hence, "dilution" by mixing with another species, in this case alkanes, will be a favorable process. In addition, the lone pair repulsion between adjacent ethers in the pure monolayer will be expected to give rise to some distortion of the monolayer structure to minimize the lone pair repulsions, which in turn may perturb the optimal interaction of the ethers with the surface. Padowitz and Messmore[13] explain the 60° tilt of hexadecyl ether molecules with respect to the lamellar axis that decreases the proximity of adjacent oxygen atoms to one another as the manifestation of such lone pair repulsions.

Nishino et al.[18] have reported that diether molecules are adsorbed with the plane of the carbon backbone perpendicular to the surface by an ingenious use of diethers with odd and even alkyl chain length spacers. This perpendicular orientation of the molecule would disrupt the adsorption of the ether since the ether could not register locally on the graphite basal plane.[33] Padowitz et al.[14] have inferred that an adsorbed alkane monolayer of tritriacontane (C_{33}) is more stable than a monolayer of the ether of the same length, hexadecyl ether, from measurement of the surface residence times of coadsorbed hexadecyl sulfide tracers. Hence, we conclude that the combination of the lone pair repulsions and the surface orientation of the ether molecules

are likely explanations for the favorable adsorption of alkanes over ethers to the graphite surface.

The calorimetry data also allows us to consider the bulk mixing behavior of the ethers and alkanes. In short, we find that all of the DBE/alkane systems, except for DBE/heptane, are essentially completely phase-separated in the solid state with a pronounced eutectic minimum. Phase separation was ascertained by the agreement of a simple depression of freezing point model on the basis of complete phase separation[32] with the data and also by the temperature invariance of the DBE solid−solid phase transition or the odd-alkane rotator transition (e.g., for DBE/nonane and DBE/undecane). The DBE/heptane system is interpreted as exhibiting strongly nonideal mixing in the bulk solid state as indicated by the continuous temperature variation of the bulk heptane rotator (solid−solid) transition with composition and a significant minimum in the liquidus curve. This behavior is somewhat surprising given that DBE and heptane might be expected to be more dissimilar in molecular form than the similarly sized DBE and nonane, and hence packing in the DBE/heptane crystal would be expected to be more difficult than for DBE/nonane (which do not appear to mix at all). At present, we have no definitive explanation for this interesting trend in behavior. However, as alluded to above, the bulk solid−solid phase transition (rotator) for heptane is only observed in the presence of graphite, suggesting that the bulk material is subtly affected by the substrate. One potential explanation is that the majority of the bulk frozen heptane is adsorbed to the graphite in some way resulting in a slightly expanded lattice. This extra room would permit both formation of a rotator phase and slightly enhanced mixing with other molecules not normally observed in bulk heptane. However, adsorption of alkanes onto graphite is usually expected to result in a compression of the crystal lattice, not expansion.

To summarize the findings discussed so far, all of the DBE/alkane monolayers studied, except DBE/nonane, are essentially phase-separated. The DBE/nonane monolayers show good, essentially ideal mixing. All of the DBE/alkane bulk mixtures exhibit phase-separated behavior, except DBE/heptane which shows strongly nonideal mixing. We propose that the mixing behavior in the DBE/nonane monolayers is due to reduced repulsions between ether oxygen lone pairs by dilution with the alkanes. If dilution of the lone pair repulsions was the only effect, then any alkane would exhibit mixing with the ether. However, because ideal mixing is only observed for nonane and DBE, this clearly indicates that there must also be effective molecular packing of molecules of approximately the same size (nonane and DBE have essentially the same molecular footprint).

In addition, both the odd alkanes (nonane and heptane) and longer chain symmetrical ethers prefer to form lamellae of parallel molecules in the solid monolayers, although at different angles with respect to the lamellar axis.[13−17,31] Given that DBE is also a symmetrical ether, although much shorter, it is not unreasonable that it may also adopt lamellae of parallel molecules in the solid layer. This would suggest that the relative orientation of the alkane and ether molecules is sufficiently similar that one molecule can replace the other in the adsorbed layer. Hexadecyl ether has been observed by STM to conform to the odd alkane-type lamellar structure adopted by hexadecyl sulfide ($C_{16}SC_{16}$) in a mixed monolayer of hexadecyl sulfide and hexadecyl ether with a 1:5 to 1:15 surface ratio,[13] suggesting that in a mixture of DBE and nonane the DBE might be able to similarly conform to the nonane surface structure (i.e., molecules at 90° relative to the lamellar axis). This would account for the

mixing in the DBE/nonane monolayer and the small degree of nonideal mixing seen in the DBE/heptane monolayer.

A comparison of nonane/heptane and DBE/heptane odd/odd chain length mixtures shows that the mixing in the DBE/heptane system is indeed better ($\Omega/2RT = 0.75$) than mixing in the nonane/heptane system ($\Omega/2RT = 0.97$[1]), although there is considerable experimental uncertainty. This supports the supposition that the dilution of the oxygen lone pair repulsions of the ethers by alkanes enhances the mixing of the two species in the monolayer.

The fact that the monolayer of DBE and nonane exhibits good mixing when the bulk mixture does not is interesting. There may simply be a mismatch in the 3D crystal structures of the DBE and nonane, where their 2D structures are sufficiently similar to allow mixing. We can estimate the likely extent of 3D mixing from a quantitative model used in bulk binary mixtures of organic crystals.[34,35] This model measures the similarity of the unit cells of two components in a mixture as the isomorphism coefficient

$$I = 1 - V_{un}/V_{com}$$

where V_{com} is the volume due to the overlapping parts (when the two unit cells are positioned so as to achieve maximum overlap) and V_{un} is the volume due to the nonoverlapping parts.[34] To our knowledge, the only short-chain linear symmetrical ether of relevance to this study for which a bulk crystal structure exists is diethyl ether (C_2OC_2).[36] The bulk crystal structure of diethyl ether was determined from X-ray diffraction at 128 K to be orthorhombic of space group $P2_12_12_1$ with eight molecules per unit cell. The all-carbon analogue of diethyl ether, pentane, also has an orthorhombic unit cell of space group *Pbcn* and four molecules per unit cell at 90 K.[37] Because of the difference in the number of molecules in the unit cells, the isomorphism coefficient was calculated for two unit cells of pentane and one unit cell of diethyl ether. Complete demixing in the solid phase is predicted for isomorphism coefficients below approximately 0.76, with complete mixing observed above 0.88.[35] The value of 0.51 for diethyl ether and pentane predicts complete demixing in the solid phase because of the mismatch in the crystal structures of the two components.

The differences in chain length between DBE and the alkanes shorter than nonane are considered to be sufficiently large to prevent the effective packing of the molecules in the monolayer, resulting in surface phase separation. In addition, the incompatibility of the herringbone (zigzag) crystal structures adopted by the even alkanes octane and hexane on graphite[30] with the assumed tilted lamellar structure of DBE will also be expected to contribute to the poor mixing between DBE and these alkanes in the monolayer, in a fashion similar to the plane group mismatch between even and odd alkanes such as octane and nonane.[8,38]

The regular solution model used to quantify the mixing in these systems assumed that the adsorbed liquid solutions in equilibrium with the solid adsorbed mixtures were ideal. However, mixtures of DBE and alkanes are known to be nonideal in the bulk liquid from the results of Benson et al.[39] and are unlikely to be ideal on the surface. In the regular solution model, nonideal behavior in the adsorbed liquid mixture will have the effect of reducing the value of Ω experimentally determined.[1] Thus, the Ω values reported here should be considered lower estimates. For bulk DBE + heptane, the reported maximum value of the excess molar enthalpy of 120 J mol^{-1} at $x_{DBE} = 0.5$ and 298.15 K[39] corresponds to a value of $\Omega = 480$ J mol^{-1} if mixing in the bulk liquid and the liquid
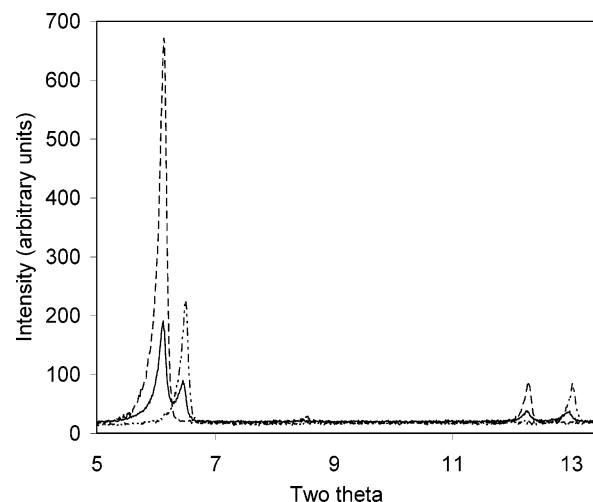

Figure 5. Experimental X-ray diffraction patterns from bulk DHE ($-$ $-$ $-$), dodecane ($-$ $-$ $-$ $-$ $-$ $-$), and an $x_{DHE} = 0.49$ mixture of DHE and dodecane ($---$), illustrating bulk phase separation.

monolayer are taken to be the same. There also may be excess entropy contributions, but these contributions are generally much smaller than the excess enthalpy.[1] However, it is expected that nonideal mixing will be most pronounced in the solid monolayer relative to the 2D or 3D liquid phases.

Another specific case where the relative size ratio is zero was also studied, the mixture of dipentyl ether (C_5OC_5, DPE) and undecane (C_{11}). Like DBE/nonane, DPE/undecane shows phase separation in the bulk solid and essentially ideal mixing in the solid adsorbed monolayer. Again, we find that the undecane is preferentially adsorbed over the DPE.

Dihexyl Ether and Dodecane Mixtures. In the DBE/alkane series, the monolayer phase behavior changed drastically from ideal mixing for nonane (relative size ratio $= 0$) to nearly phase-separated for octane with a relative size ratio of 0.12. The mixture of dihexyl ether (C_6OC_6, DHE) and dodecane (C_{12}) provided data for an intermediate relative size ratio of 0.08.

The phase separation of the bulk DHE/dodecane solid, indicated by calorimetry, was verified by X-ray diffraction as illustrated in Figure 5 where the diffraction patterns for each of the pure compounds and an $x_{DHE} = 0.49$ mixture at 200 K are plotted. Significantly, peaks characteristic of each of the pure compounds appear in the pattern of the mixture, clearly indicating phase separation of the bulk mixture. In addition, the intensity of the peaks for the mixture are approximately half that of the peaks for the pure materials, as expected.

Surprisingly, and in marked contrast to the bulk behavior, the DHE and dodecane were observed to mix in the solid monolayer. Evidence for this came from two factors: (1) the temperature variation of the monolayer melting point and (2) the temperature variation of the well-established solid–solid monolayer phase transition of the dodecane[7] over a range of bulk compositions, both shown in Figure 6. When the monolayer melting points were fitted with the regular solution model, the interaction parameter Ω was found to be much lower than the phase separation criteria $2RT$ (Figure 4a), indicating that there was mixing in the monolayer although the presence of a weak minimum, and $\Omega > 0$, indicates that the mixing was nonideal.

The depression in temperature of the solid–solid phase transition of the pure dodecane monolayer also strongly indicates good mixing in the monolayer. The solid–solid phase transition is usually very sensitive to the local environment of the alkane. If the dodecane is phase-separated into a patch of pure dodecane, the transition temperature will not change with composition.
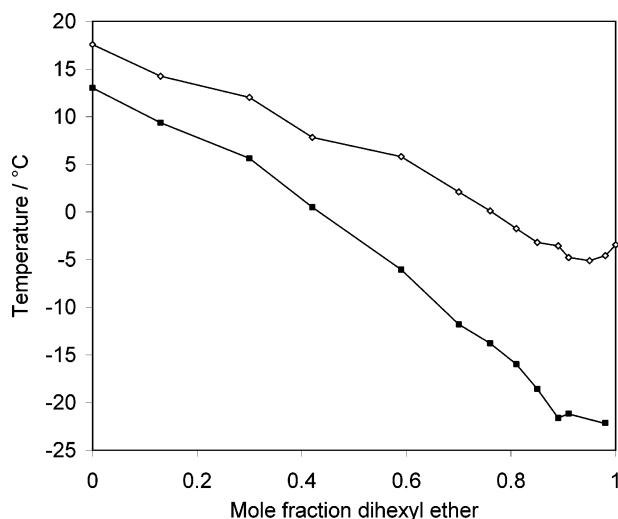
Mixing Behavior of Ethers and Alkanes

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Figure 6. Experimental monolayer phase diagram for the DHE/dodecane system showing the solid−solid monolayer phase transition of the dodecane (squares) and the melting of the solid monolayer (open diamonds).

However, if the environment of the dodecane molecules is changed by proximity to ether molecules in a mixed monolayer, the transition temperature will be expected to vary with composition, as observed.

The fact that this combination of "long" molecules (13 vs 12) which differ by a single atom can mix, when the shorter combination of DBE/octane (9 vs 8) does not, clearly indicates that the relative difference in chain lengths is the controlling parameter, not the absolute difference in chain lengths. It is also evident that a relative size ratio of between 0.08 and 0.12 is the maximum difference that can be accommodated by the monolayer crystal structures.

The experimentally determined K value for DHE/dodecane indicated preferential adsorption of the dodecane on the graphite surface, consistent with the other mixtures reported here.

Conclusion

The formation of solid monolayers by the short linear symmetrical ethers dibutyl ether, dipentyl ether, and dihexyl ether adsorbed from their liquids has been demonstrated. Mixtures of dibutyl ether and alkanes were observed to strongly demix and essentially phase-separate in the monolayer if the chain length difference was one or more atoms with good mixing for molecules of the same chain length. For the longer pair of dihexyl ether and dodecane, which differ by a single unit, nonideal mixing was observed on the graphite surface. This suggests that there is a maximum relative size mismatch between 0.08 and 0.12 above which there is no significant monolayer mixing. We find that the monolayer mixing behavior generally reflects the bulk behavior. However, there is evidence of significant differences, particularly DBE/nonane and DHE/dodecane, where the monolayer is found to mix when the bulk does not. The mixing behavior has been interpreted in terms of the sizes of the adsorbed molecules, their monolayer packing, and the mutual repulsion of adjacent ether oxygens.

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