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Spectroscopic evidence for acid-base interaction driven interfacial segregation

Saranshu Singla,[‡a] Michael C. Wilson,[‡a] and Ali Dhinojwala[*a]

Quantification of interfacial composition and interfacial energy is essential for understanding prevalent phenomena such as purification and adhesion. However, for high-energy planar solid surfaces, traditional approaches for determining both parameters are inadequate. We take advantage of interface-sensitive spectroscopy to calculate the interfacial composition for acetone-chloroform, tetrahydrofuran-benzene, and N, N-dimethylformamide (DMF)-benzene mixtures. We calculate the differences in interfacial energy for the two components of each mixture from the adsorption isotherms and compare with that obtained from acid-base and dispersive interactions. The interfacial energy calculated using interfacial segregation agrees with the interfacial energy calculated by acid-base and dispersive interactions. The comparison illustrates how molecular interactions control macroscopic interfacial segregation. In all three mixtures, acid-base interactions dominate interfacial segregation. Comparing the two approaches for DMF-benzene mixtures leads to evidence of DMF dimerization in benzene. Using the present approach, the interfacial composition and interfacial energy can now be understood for interfacial behaviors including wetting and self-assembly.

Introduction

The composition of the liquid-mixture/solid interface influences performance across a myriad of technological areas, including medicine, filtration, and electronics.[1–4] The adsorption of biological molecules on a medical device surface dictates its success or failure.[1] The preferential adsorption of dye molecules to an adsorbent allows for the separation of dye from aqueous solutions.[2] The organization of molecules at the electrode/electrolyte interface affects the performance of batteries.[3,4] Experimental quantification and theoretical prediction of liquid-mixture/solid interfacial composition is essential for improving device performance.

Numerous techniques (gravimetric, spectroscopic, and volumetric) and adsorption theories (notably from Langmuir and from Defay and Prigogine) have been developed to examine the interfacial composition.[5–8] For high-energy planar solids, the relation between experiment and theory has remained challenging because of difficulties in the quantification of interfacial composition and interfacial energy.[9,10] The aforementioned techniques require high surface area materials to determine interfacial composition. Additionally, the interfacial energy, a parameter used in the Defay-Prigogine adsorption model, cannot be calculated

for high-energy solids using contact angle, calorimetry, or previous theories (Good-Girifalco, Owens-Wendt, Wu, and van Oss-Chaudhury-Good).[10–14] New methods must be utilized to determine the interfacial composition and interfacial energy of the liquid-mixture/high-energy solid interface.

In this work, we examine interfacial composition and interactions using interface-sensitive sum frequency generation (SFG) spectroscopy for adsorption from acetone-chloroform, tetrahydrofuran (THF)-benzene, and N, N-dimethylformamide (DMF)-benzene mixtures on sapphire. SFG, a second-order non-linear optical technique, provides information about molecular vibrations selectively at an interface, where there is a breakdown in inversion symmetry.[15] While SFG has been utilized to quantify both interfacial composition and interactions, these have not be integrated into a coherent approach based on thermodynamics.[16–19]

We consider the role of acid-base interactions in controlling interfacial segregation by analyzing SFG results using two independent approaches. First, we utilize the shifts in the sapphire surface hydroxyl peak positions in contact with binary mixtures to calculate the adsorption isotherm. The adsorption isotherms are analyzed using the Defay-Prigogine thermodynamic adsorption model to extract the difference in interfacial energies of each component with sapphire.[7,8] Independently, the SFG data for pure liquids is used to measure the strength of the acid-base interactions. The acid-base interactions are added to the dispersive interactions to obtain interfacial energies by combining the Dupré and

[a] Department of Polymer Science, University of Akron, Ohio 44325.
‡ These authors contributed equally to this work
∗ Email:ali4@uakron.edu

Fowkes approaches.[20,21] The agreement in the interfacial energies measured from adsorption and the Dupré-Fowkes approach validates the applicability of the Dupré-Fowkes approach and reveals the importance of acid-base interactions in controlling interfacial segregation at liquid/high-energy solid interfaces. This generalized approach can now be applied to other liquids, polymers, and biomolecules such as proteins, peptides, and lipids.

Results and Discussion

The SFG spectra in the hydrocarbon region (2800–3150 cm^{-1}) are shown in Figure 1 for both pure components and different mixtures of acetone-chloroform, THF-benzene, and DMF-benzene. SFG selectively probes molecular vibrations at the interface. For the acetone-chloroform binary mixture (Figure 1A), the acetone signature ($\sim$2930 cm^{-1}, s-CH$_3$ vibration (Table S2)) is observed at the interface for concentrations greater than 1 mole % of acetone. As the acetone molar concentration increases, the relative intensity of the acetone peak increases with respect to the chloroform peak ($\sim$3028 cm^{-1}, C-H vibration (Table S2)). Similarly, at concentrations greater than 1 mole % of THF from THF-benzene binary mixtures, we observe segregation of THF molecules at the interface (Figure 1B). Interestingly, for the DMF-benzene binary mixtures, the DMF peak ($\sim$2940 cm^{-1}, s-CH$_3$ vibration (Table S2)) appears at concentrations as low as 0.01 mole % of DMF. As the molar concentration of DMF increases, the DMF peak increases relative to the benzene peaks, reflecting the increasing number of DMF molecules segregated to the sapphire surface.

SFG intensity is proportional to both the concentration and the orientation distribution of interfacial functional groups.[22] Previously, researchers have calculated the interfacial concentrations using the hydrocarbon region by comparing the intensities of peaks attributed to different components and by confirming that the orientation distribution of the functional groups does not change with concentration.[18] Due to the change in orientation distribution of benzene molecules (seen in the varying ratio of different benzene peaks) as a function of bulk concentration for THF-benzene and DMF-benzene mixtures, the determination of interfacial concentrations from the hydrocarbon region requires investigation of the orientation distribution using molecular dynamics simulations.[23] However, since the orientation distribution of the sapphire surface hydroxyl groups are not expected to change with concentration (Figure S1), the hydroxyl region could be used to calculate interfacial concentrations on sapphire as shown by Prasad *et al.*[19,24] The surface free hydroxyl peak of sapphire is typically observed around 3710 cm^{-1}. When brought in contact with different liquids, acid-base interactions induce the peak to shift to lower wavenumbers.[16,25] Thus, peak shift (or frequency shift) can be used as an identifying characteristic for a given molecule to calculate interfacial concentrations on sapphire.[19]

The SFG intensity is plotted as a function of frequency shift (relative to the sapphire free-hydroxyl peak) for both pure components and different mixtures of acetone-chloroform, THF-benzene, and DMF-benzene (Figure 2). The absolute peak position of the shifted sapphire hydroxyl peak in contact with differ-

ent liquids or liquid mixtures could vary across experiments as a result of variation in the position of the sapphire free-hydroxyl peak at the sapphire/air interface (Figure S2). However, frequency shift, a measure of the strength of interactions between sapphire and molecules in contact, remains constant across experiments. Therefore, frequency shift was selected instead of wavenumber to plot the SFG data in the hydroxyl region. Clearly, acetone, THF, and DMF result in a higher frequency shift relative to chloroform or benzene, signifying stronger acid-base interactions. For the acetone-chloroform binary mixture with 0.1 mole % of acetone (Figure 2A), a single peak centered at $\sim$30 cm^{-1} (similar to pure chloroform, Table S1) is observed. As the acetone concentration increases, the spectral shape changes and visually appears bimodal, similar to pure acetone, suggesting preferential segregation of acetone molecules next to sapphire. A similar trend is observed for the THF-benzene mixture (Figure 2B). Correlating with the hydrocarbon region, for DMF-benzene, the spectral shape starts changing at concentrations as low as 0.01 mole % of DMF, indicating the stronger segregation of DMF molecules compared to THF next to the sapphire surface in benzene (Figure 2C).

To calculate the relative interfacial concentrations of the two liquids at the sapphire surface, the SFG intensity vs. frequency shift data (Figure 2) was analyzed with three Lorentzian peaks (one peak for chloroform or benzene and two for acetone, THF, or DMF). The detailed fitting procedure is described in the Fitting Mixture Spectra section in the Supporting Information. The intensity ratio for the bimodal peaks of acetone, THF, or DMF is kept constant for each concentration. The interfacial concentrations were determined by comparing the amplitudes, A$_q$, for peaks attributed to the individual components of the binary mixture. The A$_q$ derived for each component reflects the number of sapphire surface hydroxyl groups interacting with the component. However, each kind of molecule could interact with a different number of sapphire surface hydroxyl groups. Thus, the ratio of A$_q$s for the two components does not necessarily represent a mole fraction but instead represents an interfacial area fraction (Equation S2). Interfacial area fractions were further converted into interfacial volume fractions through the use of literature values for the area per adsorbed molecule and the molar volume (Tables S8-S11).[26–28]

The interfacial volume fraction of the strongly segregating component is plotted as a function of the bulk volume fraction of the same component (Figure 3). As discussed earlier, acetone, THF, and DMF molecules segregate preferentially to the sapphire surface relative to chloroform and benzene molecules due to stronger interactions between the acetone, THF, or DMF molecules and the sapphire surface hydroxyl groups. The adsorption isotherm is analyzed using the Defay-Prigogine adsorption model. The model considers an equilibrium between surface and bulk phases. By equating the chemical potentials of each component in the two phases, the surface concentrations are related to the macroscopic surface energy. This model was later extended to liquid/solid interfaces by Everett and can be reduced to the form of the Langmuir model for ideal solutions. To consider the interactions between the liquid molecules, we employ a parallel-layer non-
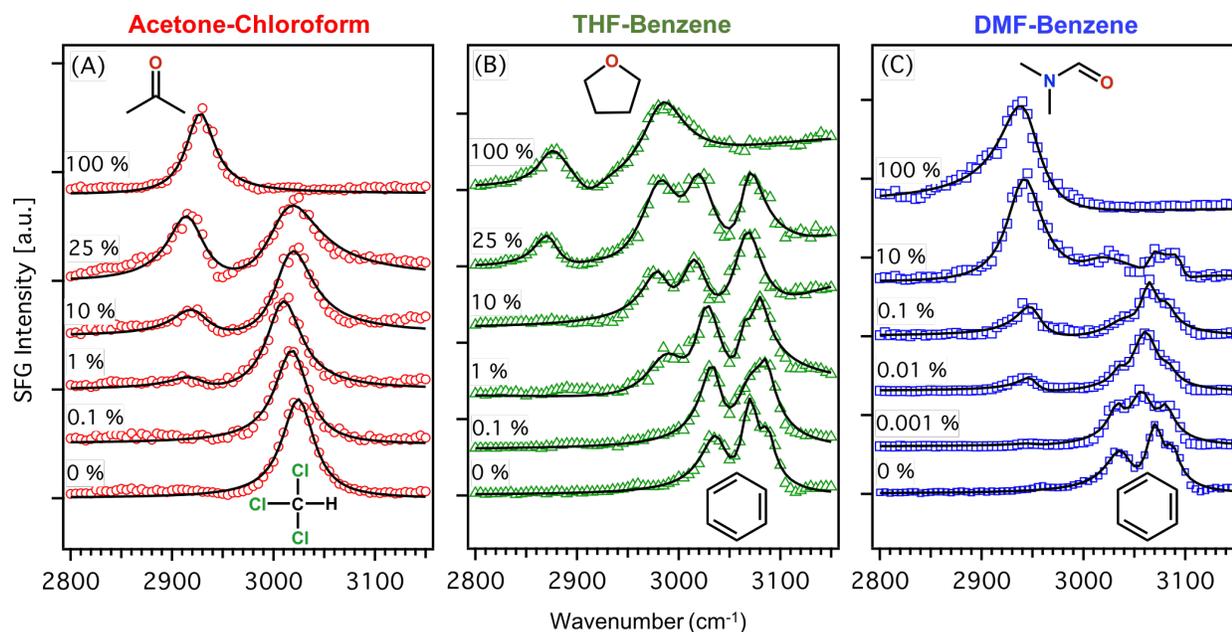
Fig. 1 SFG spectra collected using PPP (P-polarized SFG, P-polarized visible, and P-polarized infrared) polarization in the hydrocarbon region (2800–3150 cm^{-1}) for different bulk concentrations given in mole % of (A) acetone (acetone-chloroform), (B) THF (THF-benzene), and (C) DMF (DMF-benzene). The spectra have been visually normalized with respect to the chloroform (acetone-chloroform) or benzene (THF-benzene and DMF-benzene) peaks and vertically offset for clarity. The solid lines represent the fitting curves using the Lorentzian equation (Equation S1).
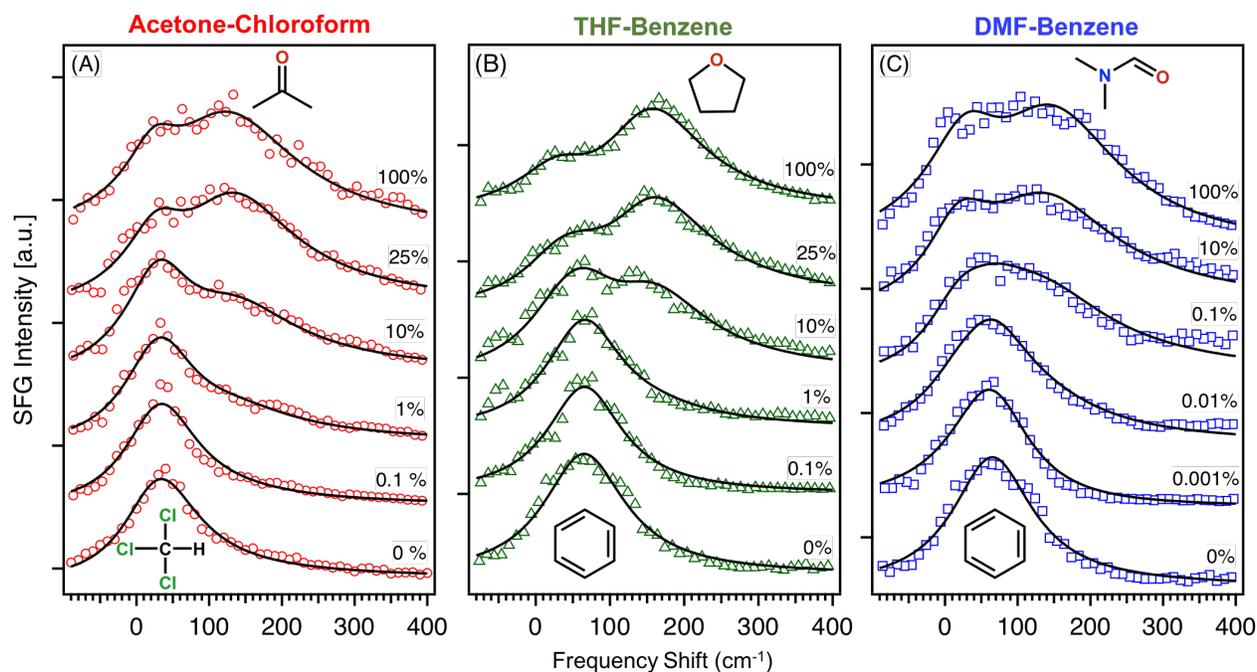
Fig. 2 PPP SFG intensity plotted as a function of frequency shift (relative to the sapphire free-hydroxyl peak, cm^{-1}) for different bulk concentrations given in mole % of (A) acetone (acetone-chloroform), (B) THF (THF-benzene), and (C) DMF (DMF-benzene). Each spectrum was normalized with respect to the observed maximum SFG intensity for that spectrum. The spectra have been vertically offset for clarity. The solid lines represent the fitting curves using the Lorentzian equation (Equation S1).
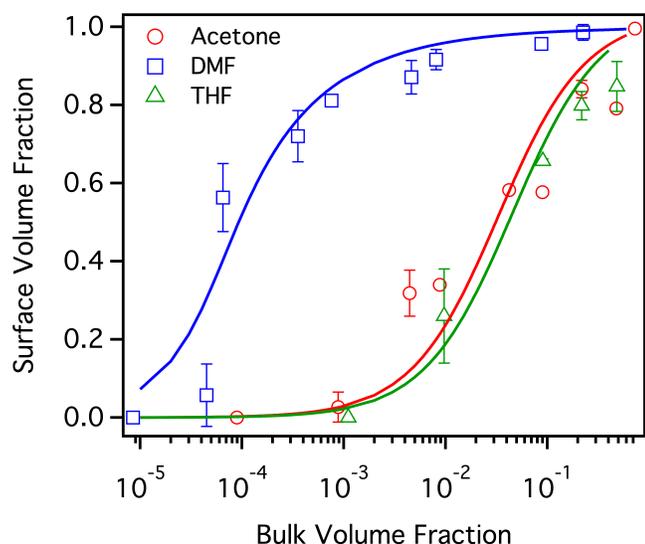
Fig. 3 Adsorption isotherms of acetone, THF, and DMF on sapphire from binary mixtures of acetone-chloroform, THF-benzene, and DMF-benzene, respectively. The error bars represent ±1 standard deviation of the two individual repeats. The solid lines represent the fitting curves obtained using the Defay-Prigogine adsorption model with $r = 1$ for acetone-chloroform and THF-benzene, and $r = 2$ for DMF-benzene.

athermal Defay-Prigogine adsorption model (Equation 1) for a mixture of molecules (1 and 2) with differing sizes against a solid (s), in which one species has r connected lattices sites.[8,29] The variables $\phi_{1,m}$ and $\phi_{1,l}$ are the interface and bulk volume fractions of the liquid 1. In addition, l and m describe the fraction of neighbors in the same and adjacent layers, respectively, and can be calculated based on the molecular packing. A value of $l = 0.5$ and $m = 0.25$ was used assuming a close-packed lattice that satisfies the condition $l + 2m = 1$.The interactions between liquids 1 and 2 are described using the interaction parameter (α), which can be obtained from the Hildebrand solubility parameters (Equation S10). The terms γ_{1s} and γ_{2s} are the interfacial energies between the solid (s) and liquids 1 and 2, and a is the area of one mole of molecules. We calculate ($\gamma_{2s} - \gamma_{1s}$) using Equation 1, as all other parameters are known (Table S11).

$$RT\ \ln\left(\frac{(\phi_{1,m})^{\frac{1}{r}}}{1-\phi_{1,m}} \cdot \frac{1-\phi_{1,l}}{(\phi_{1,l})^{\frac{1}{r}}}\right) + 2\alpha l\ (\phi_{1,l}-\phi_{1,m}) - \alpha m\ (1-2\phi_{1,l})$$
$$= (\gamma_{2s}-\gamma_{1s})a \quad (1)$$

To elucidate the correlation between intermolecular interactions and competitive adsorption on a high-energy planar sapphire surface, we also calculate the difference in interfacial energies of liquids 1 and 2 with sapphire ($\gamma_{2s} - \gamma_{1s}$ or $\Delta\gamma$) by combining equations proposed by Dupré and Fowkes. The Dupré equation defines the work of adhesion (W), the free energy required to separate two continuum slabs in vacuum, as the sum of the surface energies of the two materials (γ_i and γ_j) minus the interfacial

energy between them (γ_{ij}) (Equation 2). Applying Equation 2 to each liquid, $\Delta\gamma$ can be written in terms of the surface energies of the two liquids (γ_1 and γ_2) and the difference in the works of adhesion ($W_{2s} - W_{1s}$ or ΔW) (Equation 3).

$$W = \gamma_i + \gamma_j - \gamma_{ij} \quad (2)$$

$$\Delta\gamma = (\gamma_2 - \gamma_1) - (W_{2s} - W_{1s}) = (\gamma_2 - \gamma_1) - \Delta W \quad (3)$$

The Fowkes equation defines the work of adhesion as the sum of the dispersion (W^{LW}) and acid-base (W^{AB}) works of adhesion (Equation 4) from which W_{1s} and W_{2s} can be calculated.[21] The Lifshitz theory allows for calculation of W^{LW} (Equations S3 and S4) entirely from parameters listed in the literature, while W^{AB} can be determined (Equation S5) by multiplying the number of interfacial acid-base pairs (n) with the enthalpy of interactions (ΔH), calculable by the Drago-Wayland equation (Equation S6) or the Badger-Bauer rule (Equation S7).[14,20,21,25,30] The surface energy values (γ_1 and γ_2) can be obtained from the literature and hence $\Delta\gamma$ can be calculated.[28]

$$W = W^{LW} + W^{AB} = W^{LW} + n\ (\Delta H) \quad (4)$$

The $\Delta\gamma$ values calculated using the Defay-Prigogine adsorption model with $r = 1$ (equal molecular size for the two components) for acetone-chloroform and THF-benzene agree reasonably well with the $\Delta\gamma$ values obtained using the Dupré-Fowkes approach, as seen in Table 1. In comparison to acetone-chloroform and THF-benzene, the DMF-benzene mixture shows unexpectedly higher interfacial segregation. The difference in frequency shifts for the two components of each binary mixture is similar (83±13, 66±16, and 57±17 cm^{-1} for acetone-chloroform, THF-benzene, and DMF-benzene, respectively). Therefore, the difference in the sapphire-liquid interaction strength between the component pairs is similar for the three binary mixtures. Utilizing the Defay-Prigogine adsorption model alone would suggest a significantly higher $\Delta\gamma$ for DMF-benzene than acetone-chloroform and THF-benzene.

To resolve this discrepancy, we consider the self-associative behavior of DMF in benzene by varying the r parameter in the Defay-Prigogine adsorption model. Self-associating liquids can be defined by the presence of an acid-base component of surface energy, which suggests self-associative interactions between acidic and basic sites on the molecules.[32] The self-associating behavior of DMF is reflected in the relatively higher acid-base component of surface energy (γ^{AB}/γ) for DMF (0.18) compared to acetone (0.04) and THF (0.0).[32] Thus, we use $r = 2$ for the DMF-benzene mixture to account for possible dimerization. The value for r is estimated, not predicted; further theoretical work could determine the extent of self-association and a specific r value. However, the experimentally obtained $\Delta\gamma$ value from adsorption aligns with the $\Delta\gamma$ predicted using the Dupré-Fowkes approach, including dimerization of DMF (Table 1 and Table S3). The agreement in the $\Delta\gamma$ suggests the dimerization of DMF dissolved in benzene, which could only be inferred upon the comparison between the two approaches.

Table 1 Interfacial energy difference ($\Delta\gamma$) determined from the Defay-Prigogine adsorption model (Equation 1) and the Dupré-Fowkes approach (Equation 4), with enthalpy calculations from both the Drago-Wayland (Equation S6) and the Badger-Bauer rule (Equation S7).

Liquid mixture	$\Delta\gamma$ Adsorption Defay-Prigogine mJ/m^2	$\Delta\gamma$ Dupré-Fowkes	
		Drago-Wayland mJ/m^2	Badger-Bauer[a] mJ/m^2
Acetone-Chloroform	49	-[b]	49$\pm$9
THF-Benzene	35	60$\pm$18	59$\pm$11
DMF-Benzene	56[c]	56$\pm$19	40$\pm$12

[a] For the bimodal peaks of acetone, THF, and DMF, a weighted average was used to calculate the frequency shift (Δv) for use in the Badger-Bauer equation (Equations S8 and S9).

[b] Chloroform does not have E_B and C_B parameters in the original Drago-Wayland framework.[31]

[c] $r = 2$ was used to obtain fit.

The Dupré-Fowkes approach enables the extraction of the relative contribution of acid-base interactions in competitive adsorption. The relative contribution of acid-base interactions to ΔW is ~83 %, ~76 %, and ~85 % for acetone-chloroform, THF-benzene, and DMF-benzene, respectively, highlighting the significance of acid-base interactions in driving interfacial phenomena.[19,33] The importance of polar interactions (of which acid-base interactions are a subset) for accurately predicting interfacial tension in polymer/polymer interfaces has been emphasized by Wu; differences in the polar component primarily induce interfacial tension.[34] Thus, acid-base interactions should be thoroughly considered when designing experiments and technologies. Understanding the acidic or basic nature of materials is critical, as exemplified in hard-soft acid-base (HSAB) theory and the Drago-Wayland framework.

Conclusion

Acid-base interactions primarily govern interfacial segregation for the mixtures studied. The interfacial composition for binary liquid mixtures on high-energy, planar sapphire is successfully quantified using interface-sensitive spectroscopy. The approach can be extended to determine the interfacial composition for a wide variety of materials. By analyzing the adsorption isotherm in light of the Defay-Prigogine adsorption model, the difference in interfacial energies of the two binary liquid components with sapphire is calculated. The difference in interfacial energies is independently calculated using the Dupré-Fowkes approach and the interfacial energies are consistent with those obtained from the adsorption experiments. Additionally, the comparison between the Defay-Prigogine and Dupré-Fowkes approaches reveals the self-association of DMF molecules dissolved in benzene. Clearly, self-association of DMF affects the adsorption behavior and could affect related phenomena.

As the Dupré-Fowkes approach is based on thermodynamics, it can be extended to other interfacial behaviors. Furthermore, the enthalpy of interactions can be obtained using not only SFG, but other techniques. The Dupré-Fowkes approach gives a metric for understanding the adhesion energy of polymeric or biological adhesives, the surface segregation of small molecules or large biomacromolecules such as proteins and polymers, and the binding constants of molecules on flat or three-dimensional molecular scaffolds. A direct approach to quantify interfacial composition and its correlation with interfacial interactions impact various fields, including chemistry, materials science, and biology.

Conflicts of interest

There are no conflicts to declare.

Author Contributions

S.S., M.C.W., and A.D. designed the study. S.S. and M.C.W. collected and analyzed the data. S.S. and M.C.W. wrote the original draft and S.S., M.C.W., and A.D. reviewed and edited the manuscript.

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