

The Role of Steric Effects in the Adsorption of Chemically Similar Probes to a Poly(methyl methacrylate) Surface

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SYNOPSIS

The role of steric effects in the adsorption of chemically similar acidic probes to the model basic surface of poly(methyl methacrylate) (PMMA) was examined using the technique of inverse gas chromatography (IGC). The results were expressed in terms of the acid-base contribution to the Gibbs free-energy change upon adsorption. The acid-base component of the adsorption free energy, computed on the basis of *theoretical* modes of adduct formation, was found to depend strongly on the molecular structure of the adsorbate, suggesting the importance of steric effects. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The interactions across the interface between a solid and an adjoining fluid phase govern the success of many processes. In composite formation, for instance, several polymers may be coated onto one another, with each polymer contributing a different characteristic to the composite. One polymer may provide structural integrity, so that the composite is not easily deformed, whereas another may be chemically inert, enabling the structure to be used in a chemically aggressive environment. Not only is a smooth uniform coating required, but strong ultimate adhesion between the polymers is crucial for proper performance. Without adequate adhesion, the layers may delaminate during use. In this and other cases, interfacial interactions play a key role in determining the success of the process and the quality of the final product.

Molecular interactions across a solid-liquid interface are described thermodynamically by the work of adhesion, defined by Dupré¹ as

$$W_a = \sigma_S + \sigma_L - \sigma_{SL} \quad (1)$$

where W_a is the work of adhesion; σ_S and σ_L , the solid and liquid surface free energies per unit area

in vacuo, respectively; and σ_{SL} , the interfacial tension between the two phases. The work of adhesion is numerically equal to the magnitude of the intermolecular interactions per unit area across the solid-liquid interface. The physical forces of intermolecular attraction are primarily representative of the ubiquitous London dispersion forces, but include a small contribution from Keesom and Debye forces. They are now known collectively as Lifshitz-van der Waals forces.² The specific or chemical forces operating across the interface are present whenever there is the possibility of sharing a proton or an electron pair between neighboring molecules or functional groups, which then lead to adduct formation. Fowkes and Mostafa proposed that nearly all chemical interactions of importance are Lewis acid-base interactions, including hydrogen bonding.³ The work of adhesion can then be written in terms of contributions from the Lifshitz-van der Waals (LW) and acid-base (AB) interactions:

$$W_a = W_a^{LW} + W_a^{AB} \quad (2)$$

The work of adhesion thus quantifies not only the extent, but also the nature of intermolecular interactions across an interface.

Although not directly measurable itself, the work of adhesion is related to a number of measurable quantities, such as surface tension or contact angle or to the results of calorimetric, spectroscopic, adsorption, and other experiments.⁴ In an important

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example of such a relationship, Dorris and Gray established a key link between the Gibbs free energy of adsorption, ΔG_{ads} , determined from vapor-adsorption measurements, and the work of adhesion.⁵ The change in Gibbs free energy upon adsorption is expressed as

$$W_a = \frac{-\Delta G_{\text{ads}}}{a_{\text{mol}}} \quad (3)$$

where a_{mol} is the molar area of the adsorbate. The simplest technique of performing vapor-adsorption measurements is that of inverse gas chromatography (IGC). The experiments are conducted in the same manner as are conventional gas chromatography, except that the column is packed with the solid to be characterized and probe liquids of known characteristics are injected into the column. The extent of interaction between the probe vapor and solid is manifested in its elution time and the shape of the chromatogram. IGC studies have been made to investigate a variety of solids, including synthetic polymers, wood pulp fibers, carbon fibers, silicas, and other materials, often following surface treatments.⁶ In this study, the technique of IGC has been used to examine the adsorption characteristics of monofunctionally acidic probe vapors onto the model basic surface of poly(methyl methacrylate) (PMMA). The chemically similar acidic probes varied in physical structure, such that comparing the relative adsorption of these probes may elucidate the role of steric effects in adsorption.

EXPERIMENTAL METHOD AND RATIONALE

Poly(methyl methacrylate) (Scientific Polymer Products Inc., lot #20) was packed into an 81.05 cm-long stainless-steel column (o.d. = 0.25 in.). The column was conditioned for 24 h at 60°C under a constant stream of carrier gas. IGC measurements were made with a Varian 3400 gas chromatograph equipped with a flame ionization detector, sensitive to 10^{-12} g. Heated pneumatics were used to maintain a constant temperature of the inlet nitrogen carrier gas (General Welding Supply Co., 99.995+% pure). The column temperature was held at $40 \pm 0.05^\circ\text{C}$. The injector and detector were operated at 175 and 200°C, respectively. The volumetric flow rate of the carrier gas was measured using a soap bubble flowmeter ($Q = 7.6 \text{ mL/min}$). Corrections were made to account for the vapor pressure above the soap

solution, as well as the temperature difference between column and room temperatures.

The probes consisted first of a series of saturated n-alkanes [(C₆–C₁₀) Aldrich, > 99% pure] used to establish the Lifshitz–van der Waals component of the surface free energy of the PMMA. The second set of probes used was a series of alkanes with varying extents of chlorine substitution (Eastman Kodak, 99.9% pure). The latter probes were all monofunctionally acidic in nature, with differing physical structures, as shown in Table I. They were expected to adsorb appreciably to the PMMA surface because of acid–base interactions between the acidic hydrogens on the probes and the carbonyl oxygens of the PMMA. It is reasoned that the single-acid monomer, chloroform, should be able to form adducts with all accessible carbonyl oxygens on the PMMA surface, whereas the various polyacid structures might be

Table I Monfunctionally Acidic Probe Molecules

Probe Molecule	Structure
Chloroform	$\begin{array}{c} \text{H} \\ \\ \text{Cl}-\text{C}-\text{Cl} \\ \\ \text{Cl} \end{array}$
Dichloromethane	$\begin{array}{c} \text{H} \\ \\ \text{Cl}-\text{C}-\text{Cl} \\ \\ \text{H} \end{array}$
1,2-Dichloroethane	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{Cl}-\text{C}-\text{C}-\text{Cl} \\ \quad \\ \text{H} \quad \text{H} \end{array}$
1,2-Dichloropropane	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{Cl}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \\ \text{H} \quad \text{Cl} \quad \text{H} \end{array}$
1,3-Dichloropropane	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{Cl}-\text{C}-\text{C}-\text{C}-\text{Cl} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$
1,2,3-Trichloropropane	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{Cl}-\text{C}-\text{C}-\text{C}-\text{Cl} \\ \quad \quad \\ \text{H} \quad \text{Cl} \quad \text{H} \end{array}$
1,6-Dichlorohexane	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \quad \quad \\ \text{Cl}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{Cl} \\ \quad \quad \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$

sterically inhibited in varying degrees from forming all the adducts that are stoichiometrically indicated. The probe liquids were stored in vials over a 8–12 mesh molecular sieve. Samples were injected into the column using a Hamilton CR-20 syringe. Elution data were collected and stored on an IBM 386 clone using Varian Star software.

The quantity measured in IGC experiments is the relative retention volume, V_N . It is defined as the amount of carrier gas required to elute the probe, and it is measured as

$$V_N = jQ(t_R - t_{\text{ref}}) \quad (4)$$

where j is the James–Martin compressibility factor,⁷ which accounts for changes in the carrier gas flow rate due to the pressure drop across the column; Q , the volumetric flow rate of the carrier gas; t_R , the retention time of the probe; and t_{ref} , the retention time of a nonadsorbing reference gas, such as methane. The retention time is measured as the time corresponding to the peak maximum for linear chromatography (linear regime of adsorption isotherm) or as the first moment of the elution curve for nonlinear chromatography (concentration-dependent adsorption or nonlinear regime of adsorption isotherm). The retention volume is directly related to the probe gas adsorption onto the solid as⁸

$$V_N = \left(\frac{\partial \Gamma}{\partial C} \right)_T A \quad (5)$$

where Γ is the amount adsorbed; C , the concentration of the solute; T , the column temperature; and A , the surface area of the solid. Typically, IGC studies are performed using the dilute sample sizes necessary for linear chromatography,^{9,10} i.e.,

$$V_N = KA \quad (6)$$

where K is the adsorption equilibrium constant for the solute in the mobile gas phase relative to the amount adsorbed. In finite-concentration adsorption, K is interpreted as the appropriate integral average: $(1/C_0) \int_0^{C_0} (\partial \Gamma / \partial C) dC$, where C_0 is the inlet concentration of the adsorbate.

From the adsorption equilibrium constant, the molar Gibbs free-energy change upon adsorption of the probe can be written as

$$\Delta G_{\text{ads}} = -RT \ln K + C_1 = -RT \ln V_N + C_2 \quad (7)$$

where R is the gas constant, and C_1 and C_2 are con-

stants dependent on the standard states of the gaseous and adsorbed states and the solid surface area, respectively. Equation (3) can then be used to relate the Gibbs free-energy change upon adsorption to the work of adhesion. For nonspecifically adsorbing probe gases, the work of adhesion is given by

$$W_a = 2\sqrt{\sigma_L^{\text{LW}} \sigma_S^{\text{LW}}} \quad (8)$$

where σ^{LW} is the Lifshitz–van der Waals component of the liquid (L) or solid (S) surface free-energy quantity. Combining Eqs. (3), (7), and (8) results in

$$-\Delta G_{\text{ads}} = RT \ln V_N = 2a_{\text{mol}} \sqrt{\sigma_L^{\text{LW}} \sigma_S^{\text{LW}}} + C_2 \quad (9)$$

A plot of $RT \ln V_N$ vs. $a_{\text{mol}} \sqrt{\sigma_L^{\text{LW}} \sigma_S^{\text{LW}}}$ for a series of nonspecifically adsorbing probes, such as n -alkanes, should result in a straight line, the slope of which is equal to $2 \sqrt{\sigma_S^{\text{LW}}}$. For probes that are capable of entering into acid–base interactions with the solid, Eqs. (2) and (3) can be combined to yield

$$-\Delta G_{\text{ads}} = a_{\text{mol}} (W_a^{\text{LW}} + W_a^{\text{AB}}) \quad (10)$$

Measurement of the acid–base probe retention volume permits direct determination of the acid–base contribution to the work of adhesion. By comparing the change in Gibbs free energy for the acid–base probe to that of an alkane of the same value of $a_{\text{mol}} \sqrt{\sigma_L^{\text{LW}} \sigma_S^{\text{LW}}}$, the difference in Gibbs free energy is due to acid–base interactions. Then,

$$W_a^{\text{AB}} = \frac{RT}{a_{\text{mol}}} \ln \left(\frac{V_N^{\text{probe}}}{V_N^{\text{alkane}}} \right) \quad (11)$$

Knowledge of the standard state is obviated, since the quantity of interest is the difference between two Gibbs free-energy changes.

For work in the region of finite concentration along the adsorption isotherm, the method of determining thermodynamic parameters is similar to that for the region of infinite dilution. A comparison of values of the Gibbs free energy of adsorption can be made, if the fractional coverage is specified. Furthermore, if Eq. (5) can be considered constant about a certain fractional coverage, the retention volumes may still be used to determine the Gibbs free energy of adsorption.

In this study, the thermodynamic parameters for the alkanes and acidic probes on PMMA were computed based on retention volume measurements at 2% coverage of the surface. Despite efforts to obtain

dilute sample sizes necessary for adsorption in the region of infinite dilution along the adsorption isotherm, the elution curves for the acidic probes were asymmetrical, indicating concentration-dependent adsorption.¹¹ Two percent coverage of the PMMA surface was then chosen for a basis of comparison of the relative adsorption of the acidic probes, since unpublished work¹² has revealed that solid surface energetics may be strongly reflective of the fractional coverage, especially for coverages less than 1.5%. The amount of probe needed to cover 2% of the surface was computed using the total surface area of the PMMA column and the probe molar areas. The specific surface area of the PMMA was determined from a single-point BET measurement using a Micromeritics FlowSorb II 2300 Apparatus ($\Sigma = 0.2 \text{ m}^2/\text{g}$). The alkane molar areas were computed according to a method adapted from Dorris and Gray.⁵ They determined a value of 0.06 nm^2 per ($-\text{CH}_2-$) group, based on experimental values for the C—C bond length and the distance between centers of ($-\text{CH}_2-$) groups in adjacent molecules. The slightly larger area occupied by the methyl groups at the ends of the alkanes was considered in this work. A value of 0.08 nm^2 per ($-\text{CH}_3-$) group was computed based on their data.

The molar areas of the acidic probes were determined assuming a spherical shape in a hexagonally packed configuration and including an empirical correction proposed by Dorris and Gray¹³:

$$a_{\text{mol}} = 1.33 \times 10^{14} \left(\frac{M}{\rho N} \right)^{2/3} \quad (12)$$

Table II Adsorbed Area of Probe Molecules

Molecule	Area (nm^2)
<i>n</i> -Hexane	0.40
Chloroform	0.34
Dichloromethane	0.30
1,2-Dichloroethane	0.34
1,2-Dichloropropane	0.396
1,3-Dichloropropane	0.39
1,2,3-Trichloropropane	0.42
1,6-Dichlorohexane	0.52

where M is the molecular weight of the probe; ρ , its liquid density; and N , Avagadro's number, and the molar area is expressed in nm^2 . Table II lists the areas of *n*-hexane and all of the acidic adsorbates.

RESULTS AND DISCUSSION

From the probe elution curves, the relative retention volumes were used according to Eq. (7) to determine the change in Gibbs free energy upon adsorption. The results were then plotted according to Eq. (9), as shown in Figure 1. From the slope of the line generated by the *n*-alkane adsorption data, a value of $\sigma_S^{\text{LW}} = 34 \text{ mJ}/\text{m}^2$ was determined for the PMMA surface. This value is in exact agreement with that computed from the raw data of independent research using wetting measurements to characterize a PMMA surface.¹⁴

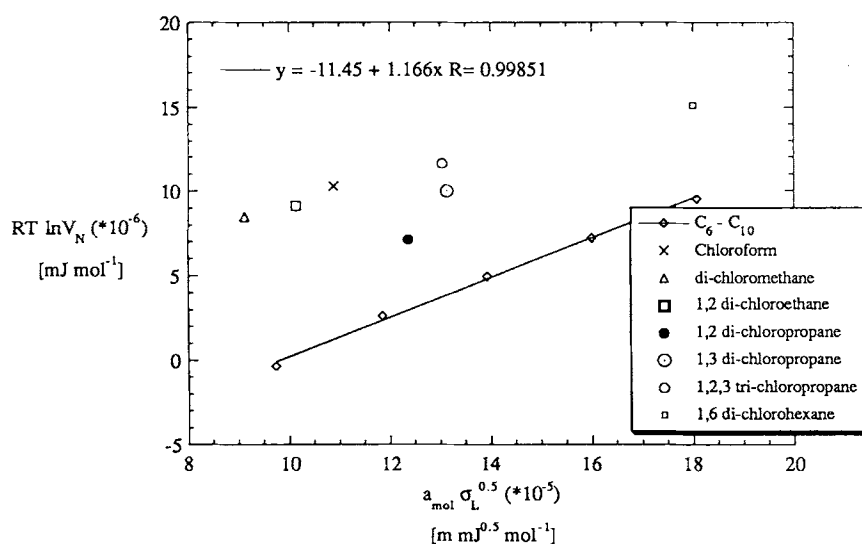


Figure 1 ΔG_{ads} of probes on PMMA at $\theta = 0.02$ (40°C).

Table III Comparison of $-\Delta G^{AB}$ Based on the Number of Possible Acid-Base Adducts

Compound	No. Possible Bonds	$-\Delta G^{AB}$ Per No. Bonds (kJ/mol)
Chloroform	1	9.0
Dichloromethane	2	4.7
1,2-Dichloroethane	2	4.4
1,2-Dichloropropane	2	2.1
1,3-Dichloropropane	2	3.1
1,6-Dichlorohexane	2	2.8
1,2,3-Trichloropropane	3	2.6

Figure 1 also shows the relative adsorption of the acidic probes compared to the *n*-alkanes. The shift from the alkane line is representative of the magnitude of the acid-base contribution to the Gibbs free-energy change upon adsorption. For all the acidic probes, there was significantly enhanced adsorption relative to the structurally similar alkanes due to acid-base interactions. The varying degrees to which these acidic probes adsorbed to the PMMA surface is attributed to differences in their structure.

By considering the ΔG^{AB} relative to the number of possible acid-base bonds between the probe and PMMA, as shown in Table III, this structural dependence is elucidated. The monomeric acidic probe, chloroform, exhibits the strongest relative adsorption to the PMMA surface. For the two other small molecules, dichloromethane and 1,2-dichloroethane, both capable of entering into two possible acid-base interactions with the PMMA, the hydrogen donors are significantly more acidic than those on the longer chain molecules that also have two possible acid-base adducts with the surface. The greater acidity of these small molecules is due to the higher number of chlorine substituents relative to the chain length. Consequently, they exhibit stronger adsorption to the PMMA surface than do the longer chain molecules that bear an equal number of hydrogen donors. For the longer molecules, the molecular configuration strongly influences the adsorption. The relative adsorption of molecules with at least one ($-\text{CH}_2-$) group between hydrogen donors is greater than for molecules with adjacent hydrogen donors, presumably because the steric hindrance caused by adjacent hydrogen donors reduces the relative adsorption. For instance, the ΔG^{AB} per possible bond for 1,2-dichloropropane is less than that for

1,3-dichloropropane. From these results, it is evident that steric effects play a significant role in the adsorption of these probes to the PMMA surface.

CONCLUSIONS

Chemically similar acidic probes of varying structure showed appreciable adsorption to the model-basic surface of PMMA. Steric effects played a significant role in their adsorption. In general, the acidic probes with the least steric hindrance adsorbed the strongest to the basic surface.

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