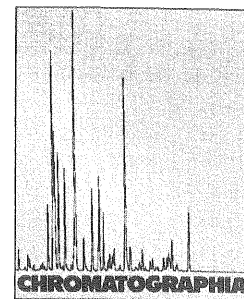


# Using Stationary Points on Potential Energy Surfaces to Model Intermolecular Interactions and Retention in Gas Chromatography



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## Abstract

The utility of electronic structure methods for studying and predicting interactions in gas chromatography is explored using a simplified model of polyethylene glycol with a homologous series of normal alcohols. Relative interaction energies were determined using stabilization energies taken at stationary points on the analyte/stationary phase potential energy surfaces using semi-empirical, *ab initio*, and density functional theory. Second order Møller-Plesset electronic structure method produced good qualitative agreement with experiment, clearly indicating the need for a model that includes weak dispersion forces.

## Keywords

Gas chromatography  
Intermolecular interactions  
Retention prediction  
Polyethylene glycol/alcohols

## Introduction

Modeling of retention and the study of fundamental retention mechanisms in gas chromatographic separations have been extremely active areas of research for several decades. A well established approach is the development of quantitative structure-retention relationships (QSRR). This methodology uses standard chemometric and statistical techniques to correlate solute descriptors with measured retention data. Numerous models have been developed for a wide variety of stationary phases and solutes [1–25]. This type of modeling has been extremely useful in the

elucidation of the intermolecular interactions responsible for retention. For example, the energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are significant descriptors for retentive processes involving electron pair donor-electron pair acceptor interaction [26], while solute properties such as carbon number, molar volume, and total energy reflect differences in dispersion interactions [2, 26, 27]. It has been shown that submolecular measures of polarity are more statistically significant in the prediction of retention than the overall dipole moment of the solute [28, 29].

In addition to increasing understanding of the intermolecular interactions responsible for retention, some rigorously derived QSRR models have predictive capabilities, and are thus useful in tasks such as the identification of unknown solutes from retention data [2]. However, the predictive value is limited; a single model is insufficient to predict retention across a wide range of stationary phase and solute chemistries.

Alternative modeling approaches include the use of molecular mechanics (MM) and molecular dynamics (MD). Retention mechanisms of alpha-pinene and tricyclene on chiral stationary phases have been investigated using MM optimizations [30]. Molecular dynamics (on MM potential energy surfaces) has also been used to study chiral recognition [31–35]. Empirical modeling of selectivity on existing stationary phase chemistries has been used in combination with MD to develop a methodology that simultaneously determines the optimum polymer composition required for the separation of specific target compounds and the optimum column dimensions. This approach has been shown to accurately calculate distribution coefficients of analytes on existing stationary phase chemistries, and has led to the development of several new phases [36–38].

Herein, we offer a unique and advantageous approach to modeling gas chromatographic retention using binding energies taken by finding stable stationary points on potential energy surfaces (PES). Due to the size of

common systems of interest, molecular dynamics studies, which allow for statistical averaging, are currently limited to PESs solved using MM. Instead, we have investigated the possibility of using stabilization energies taken at stationary points on the analyte/stationary phase PESs using semi-empirical, *ab initio*, and density functional theory (DFT). The advantage of using these levels of theory is their inherent predictive power. The trustworthiness of MM approaches is limited to systems that resemble the chemical characteristics of the systems upon which the force fields and empirical data are based. Determining a model using semi-empirical, *ab initio*, or DFT levels of theory offers the attractive opportunity to determine the selectivity of stationary phases (existing and proposed) without the restrictions of force field-based methods. Additionally, this approach is unique in the ability to increase understanding of fundamental retention mechanisms through visualization and study of electronic structure and intermolecular interactions.

The relationship given in Eq. (1) shows the dependence of the thermodynamic partition coefficient  $K$ , on the change in chemical potential,  $\Delta\mu^0$ , that occurs when a solute crosses a phase boundary in a chromatographic system [39].

$$K = e^{-\Delta\mu^0/RT} \quad (1)$$

Here,  $T$  is the absolute temperature, and  $R$  is the universal gas constant. The chemical potential can be further defined as

$$\Delta\mu^0 = \Delta H_m^0 - T\Delta S_m^0 \quad (2)$$

in which the subscript  $m$  denotes the partial molar quantities of enthalpy  $H$ , and entropy  $S$ . For chromatographic systems in which partitioning of an analyte between phases is the primary mechanism (as opposed to adsorption, etc.), the entropic contribution to the interaction energy is small, and the chemical potential is dominated by the enthalpy term [39]. The magnitude of the enthalpy term is determined by the strength of the intermolecular interactions of the analyte and the surrounding molecules. The calculation of such nonbonded interaction energies is well documented using *ab initio* methods [40, 41], and  $\Delta\mu^0$  can thus be estimated using

binding energies taken from stable stationary points on PESs.

## Experimental

Calculations were performed on a model system for analyte/stationary phase adducts. In this study, we have modeled a polyethyleneglycol (PEG) stationary phase using a diethyleneglycol molecule (PEG2). The analyte molecules considered include the homologous series  $n$ -ethanol through  $n$ -octanol.

All calculations were performed with the Gaussian suite of programs [42]. Structures were optimized using the Berny algorithm [43] at semi empirical, *ab initio*, and DFT levels. Semi-empirical calculations were performed using the PM3 method [44]. The 6-31G(d,p) basis set was used for all *ab initio* and DFT calculations [45–49]. This basis set employs an atom centered gaussian double-zeta split valence basis augmented with  $d$  functions on heavy atoms and  $p$  functions on hydrogens. *Ab initio* calculations were performed using Hartree-Fock (HF) and second order Møller-Plesset (MP2) perturbation theory [50]. DFT calculations made use of Becke's 3-parameter hybrid functional with the non-local correlation correction of Perdew and Wang (B3PW91) [51–53]. Frequency calculations were performed on the PM3, HF and B3PW91 optimized structures to verify that true PES minima had been located (i.e. all positive second derivative eigenvalues). Due to their extensive cost, MP2 frequencies were not executed; however all MP2 optimized structures exhibited similar conformational orientations as those computed and verified (with frequency calculations) at the HF and B3PW91 levels.

Interaction energies for HF and DFT calculations include both the counterpoise correction of Boys and Bernardi [54] to account for basis set superposition error and geometric relaxation according to

$$E_{int} = E_{sa} + (E_{sf} + E_{af}) - (E_s + E_a) - (E_{sf}^* + E_{af}^*) \quad (3)$$

where  $E_{sa}$  is the total interaction energy of the stationary phase and analyte,  $E_a$  is the energy of the analyte optimized alone,  $E_s$  is the energy of the stationary phase optimized alone,  $E_{af}$  and  $E_{sf}$  are the energies of the analyte and station phase

frozen in the adduct geometry and  $E_{af}^*$  and  $E_{sf}^*$  are the energies of the analyte and stationary phase frozen in the adduct geometry with the basis functions of the full adduct. The interaction energy expression for the MP2 [55] and PM3 calculations does not include basis set superposition error and is given by

$$E = E_{sa} - (E_s + E_a) \quad (4)$$

where  $E_{sa}$  is the total energy of the stationary phase/analyte adduct and  $E_a$  and  $E_s$  are the energies of the optimized analyte alone and PEG2 alone, respectively.

Experimental measurements of retention for the test compounds were collected using a Shimadzu GC-14A gas chromatograph operated isothermally over the range of 40 °C to 90 °C. The GC was equipped with a photoionization detector and a split/splitless injector, maintained at 200 °C. The column used was 15 m in length, 0.25 mm I.D., and 0.25  $\mu$ m film thickness (RTX-Wax, Restek Corporation, Bellefonte, PA). Hold-up times were calculated based on standard gas flow equations [39]. A Shimadzu CR-8A integrator was used for data collection.

## Results and Discussion

Despite intense research, an accurate, widely applicable model of chromatographic retention remains an elusive goal. Because of the importance of dispersion and the lack of cheap *ab initio* methods for modeling weak interactions, little has been done to model retention using electronic structure methods outside the regimes of MM and semi-empirical approaches. Previous work by others has accounted for dispersion using completely empirical models [36–38], or MM and semi-empirical methods [31–35], which employ empirical parameters to calculate energies and predict structure. In the current work we examine the possibility of using methods of higher level than MM. Since computational expense increases dramatically with the level of theory, the aim was to determine the minimum level of theory required for accurate prediction.

Using measured retention factors, chemical potentials,  $\Delta\mu^0$ , for the interaction between analytes and a given stationary phase system are easily

determined via Eq. 1. Figure 1 shows a plot of experimentally measured  $\Delta\mu^\circ$  versus carbon number for the series ethanol-octanol. Data were collected across a range of temperatures (40 °C–90 °C) and extrapolated to absolute zero. At this temperature, enthalpy difference  $\Delta H$ , and electronic energy difference  $\Delta E$ , become nearly equal (excluding zero point correction) and one can easily make comparisons between stabilization energies determined experimentally and obtained from electronic structure methods.

While an accurate representation of the stationary phase would include a sizeable 3-dimensional surface, the computational cost of such a system is unfeasible. Using PEG2 makes calculations at high levels of theory more tractable. Nevertheless, one must consider the limitations of using reduced models. In the current case, edge effects and orbital energy distributions are leading initial concerns. Edge effects arise from limiting an infinite chain/sheet to a finite size. Such effects can lead to a flawed model of the true electronic structure of the stationary phase due to a neglect of neighboring electron interactions. Additionally, the ideal geometry of the model system may fail to account for distortions due to steric interactions brought about by neighbor-neighbor repulsion in the complete system. The two forces alone, and working in concert, may provide for multiple analyte/stationary phase interactions that cannot be properly accounted for by the model system. Furthermore, the model's exaggerated ratio of polar to nonpolar regions may overestimate polar interactions.

Starting geometries of the analyte relative to the stationary phase were determined from the PEG2 central oxygen lone pair orientation and electrostatic potential. Figure 2 shows the highest occupied molecular orbital, which contains the central oxygen lone pairs and the electrostatic potential of the PEG2 model system. As one might expect, the electrostatic potential and lone pair spatial distribution are in agreement suggesting that the region for interaction with a partially positive hydrogen, such as the hydroxyl hydrogens on the analyte set, is most probable at the two lone pairs on the PEG2 central oxygen. Chemical intuition dictates, therefore, that two possible analyte/stationary phase geometries are most likely. The first orientation provides only for hydroxyl hydrogen

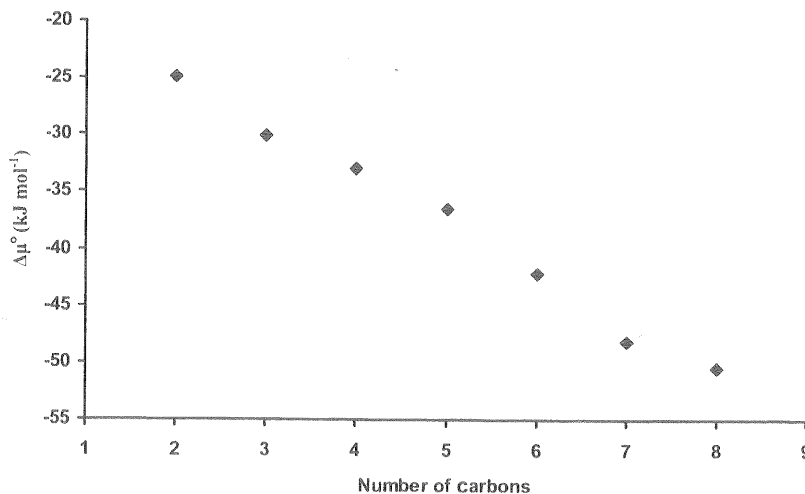


Fig. 1. Experimental values of  $\Delta\mu^\circ$  for homologous alcohols on a PEG column

bonding to the PEG2 central oxygen lone pair (see Fig. 3a); the second orientation includes the additional ability for interaction between the PEG2 oxygen second lone pair and the beta carbon hydrogens (see Fig. 3b). Minimizing these two possible starting orientations led to the same final structure, namely that which allows for additional interaction of the beta analyte methylene group with PEG2 (see Fig. 3b).

Semi-empirical calculations using the PM3 method were employed to calculate the stabilization of the analyte/stationary phase adduct; results are shown in Fig. 4 and Table 1. These calculations do not capture the correct trend in stabilization. The PM3 data suggest that this level of theory might qualitatively describe the alcohol/PEG2 interactions for small analyte chains (i.e. ethanol, propanol, and butanol), but the PM3 calculations clearly begin to fail once chains with five carbons or more are considered. As shown in Table 2, there is a sharp change in hydrogen bond length from butanol to pentanol. This may be explained by the shortcomings of the level of theory. PM3 fails to accurately predict the van der Waals interactions. The small basis set used in PM3 calculations also limits its ability to capture hydrogen bonding effects, which are imperative for proper modeling of the alcohol/PEG2 adducts.

HF also fails to accurately reproduce the expected trend in stabilization for the homologous alcohol series (See Fig. 5, Table 1). Rather than predicting the experimental trend, whereby stabilization energy increases in magnitude as alcohol chain length increases, the HF results

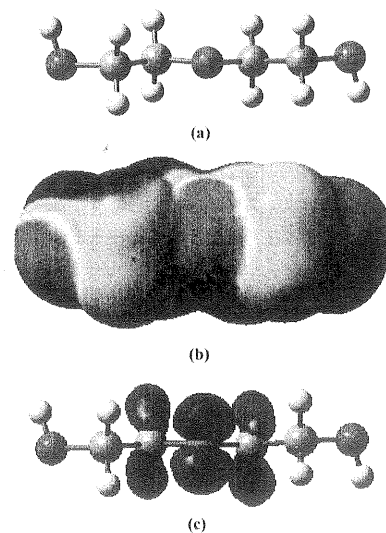


Fig. 2. PEG2. (a) Geometry. (b) Electrostatic potential. (c) Highest occupied molecular orbital showing location of central O lone pair orbitals

indicate little change in stabilization energy with respect to chain length; the total range of stabilization is ca. 0.13 kJ mol<sup>-1</sup>. We attribute this error to the fact that HF theory does not contain a dispersion interaction term. The data in Table 2 show that the hydrogen bond length is nearly the same for all of the analytes considered, which is similar to the MP2 trend. However, the HF hydrogen bond lengths are significantly longer than the MP2 hydrogen bond lengths. Given that HF is known to be able to capture significant portions of hydrogen bonding effects, we attribute this difference to weak interactions.

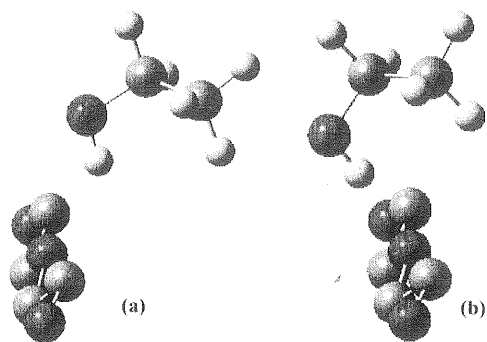


Fig. 3. Analyte/PEG2 orientation (propanol used for representative model; PEG2 hydrogens removed for clarity). (a) Orientation 1. (b) Orientation 2. See text for details

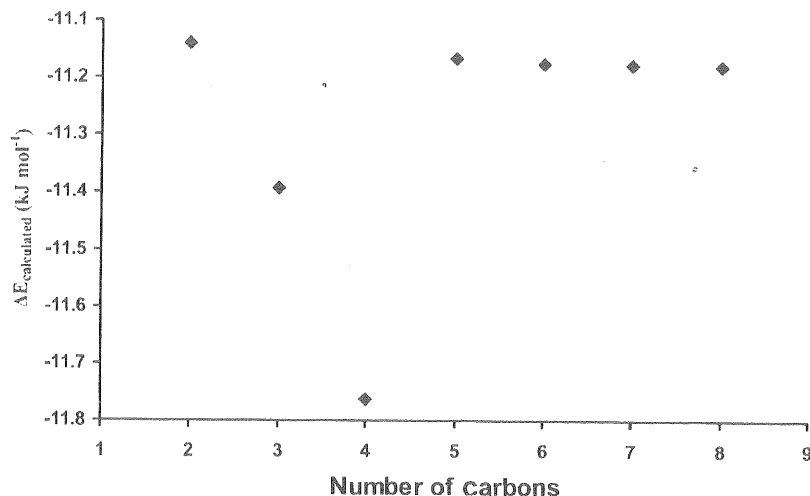


Fig. 4. Analyte/PEG2 adduct interaction energy calculated at the PM3 level of theory

Table 1. Calculated interaction energies (kJ mol<sup>-1</sup>) at PM3, HF/6-31G(d,p), B3PW91/6-31G(d,p), and MP2/6-31G(d,p) levels of theory

Level of Theory	Level of Theory			
	PM3	HF/6-31G(d,p)	B3PW91/6-31G(d,p)	MP2/6-31G(d,p)
<i>n</i> -ethanol	-11.14	-12.45	-10.66	-39.96
<i>n</i> -propanol	-11.39	-12.43	-10.33	-40.58
<i>n</i> -butanol	-11.76	-12.38	-10.41	-40.92
<i>n</i> -pentanol	-11.17	-12.35	-10.84	-41.00
<i>n</i> -hexanol	-11.17	-12.33	-10.13	-41.04
<i>n</i> -heptanol	-11.18	-12.32	-10.02	-41.05
<i>n</i> -octanol	-11.18	-12.32	-9.21	-41.08

Table 2. Hydroxyl hydrogen-PEG2 central oxygen distance (Å) in optimized geometries calculated at PM3, HF/6-31G(d,p), B3PW91/6-31G(d,p), and MP2/6-31G(d,p) levels of theory

Level of Theory	Level of Theory			
	PM3	HF/6-31G(d,p)	B3PW91/6-31G(d,p)	MP2/6-31G(d,p)
<i>n</i> -ethanol	1.843	2.028	1.930	1.878
<i>n</i> -propanol	1.842	2.027	1.922	1.875
<i>n</i> -butanol	1.842	2.028	1.921	1.876
<i>n</i> -pentanol	1.838	2.028	1.931	1.876
<i>n</i> -hexanol	1.838	2.028	1.929	1.876
<i>n</i> -heptanol	1.838	2.029	1.928	1.876
<i>n</i> -octanol	1.838	2.029	1.931	1.876

Furthermore, HF's failure to discriminate between the various analytes, leads one to deduce that electrostatic effects are not the dominant force involved in analyte/PEG interactions.

Although DFT has gained much popularity due to its inherent inclusion of dynamic correlation energy, many functionals, including B3PW91, fail to properly account for weak van der Waals forces. Consequently, the B3PW91 calculations fail to quantitatively or qualitatively predict the analyte/stationary phase adduct interaction energies (see Table 1) as compared to the MP2 results. The overall stabilization trend with respect to analyte chain length, as shown in Fig. 6, is opposite experiment. The undulations present in the stabilization energy plot roughly correspond to changes in the hydrogen bond lengths (see Table 2). This error in geometry likely precipitates from DFT's poor description of weak bond interactions.

Second order Møller-Plesset perturbation theory is the only level of theory considered here that qualitatively orders the stabilization of the analyte/stationary phase adduct in agreement with experiment (see Fig. 7), and is notably the only theoretical approach used in the study that inherently captures dispersion energy. The hydrogen bond distances throughout the homologous set of alcohol/PEG2 adducts are similar, and are shorter in comparison to the HF and DFT results. The inclusion of dispersion in the calculation is the most probable reason for the shortened O-H bond distance, as well as the qualitative agreement in stabilization energy with experiment. MP2 structures also show shorter beta methylene to PEG2 central oxygen distances. Specifically, the nearest analyte beta hydrogen to PEG2 central oxygen distances for B3PW91 structures range from ca. 3.2 to 3.4 Å, whereas those for the MP2 structures range from ca. 2.8 to 2.9 Å. Given that the C-H bond is not nearly as polarized as the hydroxyl O-H bond, this interaction is a weak intermolecular interaction, one that is not described by other levels of theory considered. The geometric changes combined with the qualitative agreement with experiment attest the importance of dispersion in the interaction of a stationary phase and analyte. Further, as discussed in the beginning of this section, one would expect quantitative errors due to the reduced size of the stationary phase

model used. For the set of analytes considered here, one would anticipate that differences in stabilization energy should decrease with increasing analyte chain length. This expectation is based on the fact that longer chain alcohols will increasingly gain a significant portion of stabilization from weak interactions with segments of the stationary phase not included in the PEG2 model. Indeed, the calculations show that the incremental change in stabilization decreases as the carbon number of the analytes increases.

A holistic analysis of the data shows that the current model, although unable to quantitatively predict the alcohol-PEG interaction energies, does qualitatively produce the proper order of separation when strong and weak intermolecular forces are included in the computational methods employed. These results demonstrate the utility of our simplistic model as a first order approximation of analyte/stationary phase interaction. Indeed, this work shows promise for the future direction of computational modeling in the field of separation science.

## Conclusion

In summary, we have introduced a model for studying GC stationary phase/analyte interactions. Using standard electronic structure methods to locate minima on the stationary phase/analyte PES, we are able to qualitatively reproduce experimental data. The computational results clearly indicate that while strong intermolecular forces (i.e. hydrogen bonding) are important in PEG/alcohol adduct formation, the ability of a GC to discriminate between a series of terminal alcohols is largely due to weak interactions (i.e. dispersion). Therefore, semi-empirical, HF, and DFT methods are inadequate and one must instead employ MP2 or higher levels of theory in order to capture the necessary dispersion forces. Additionally, the data indicate the usefulness of a simple model, namely PEG2, for the complex polymer network present in a commercial PEG stationary phase column.

As discussed earlier in the text, we emphasize the limitations of the current methodology due to the limited size of the stationary phase model. In order to gain quantitative predictive power, we suggest that one must expand the PEG model system to explicitly include a

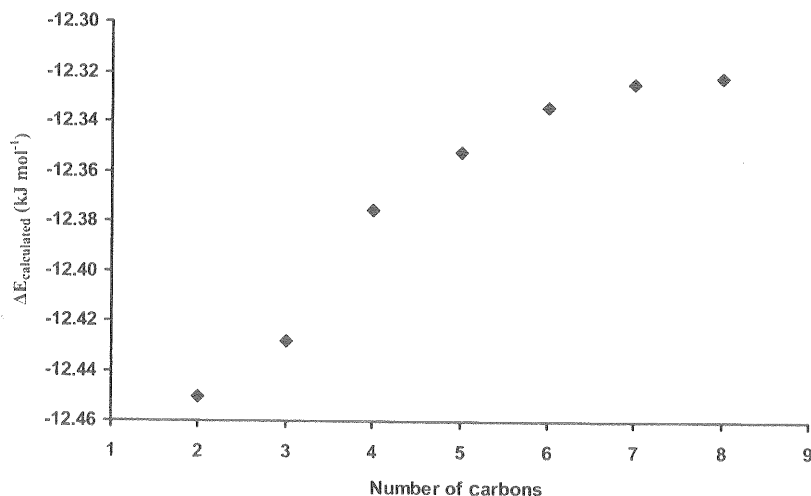


Fig. 5. Analyte/PEG2 adduct interaction energy calculated at the HF/6-31G(d,p) level of theory

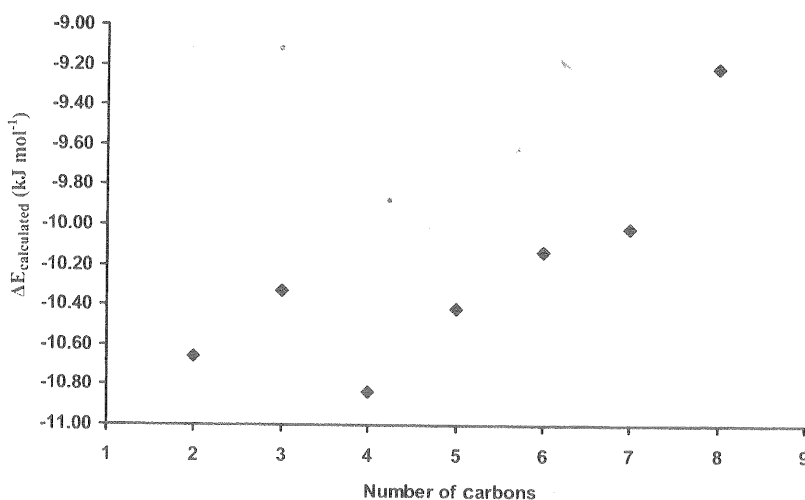


Fig. 6. Analyte/PEG2 adduct interaction energy calculated at the B3PW91/6-31G(d,p) level of theory

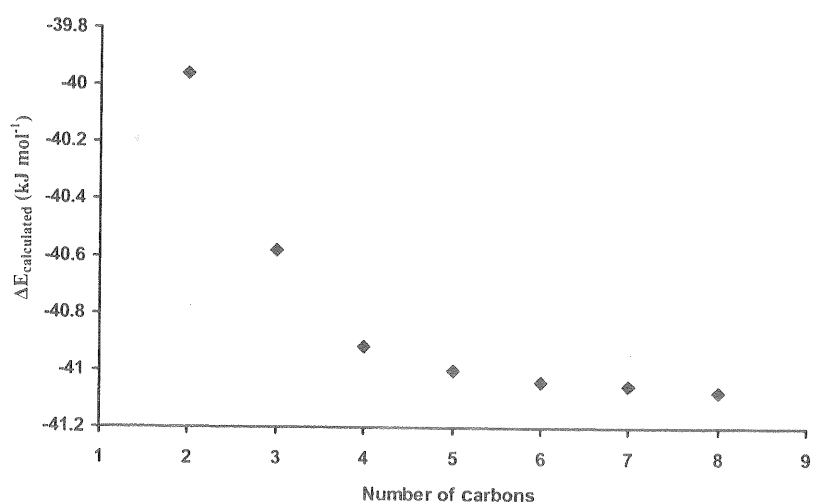


Fig. 7. Analyte/PEG2 adduct interaction energy calculated at the MP2/6-31G(d,p) level of theory

two-dimensional "sheet" or even a three-dimensional "slab" of PEG. The computational limitations associated with this necessity (keeping in mind that this study suggests that MP2 or higher level methods must be employed) make it unusable given conventional algorithms and methods. Furthermore, moving beyond PEG2 to a network of multiple polymers introduces the need to sample all energetically feasible conformations of both the isolated stationary phase system and the stationary phase/analyte adducts. If longer chain alcohols (or larger analytes in general) are considered, their various conformations must also be considered. The authors are exploring multiple means for resolving these issues so as to extend the current work to gain quantitative results while maintaining computational practicality.

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