REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

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1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE

3. REPORT TYPE AND DATES COVERED

4. TITLE AND SUBTITLE
The Development of Computational Methods of Adhesion and Adhesive Science and Technology

5. FUNDING NUMBERS
Grant No.:
N00014-90-J-1298

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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research

DTIC
ELECTE
SEP 27 1995
S D
B

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

DTIC QUALITY INSPECTED 8

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

The development of computational methods for describing the adhesive process was explored. Serious problems currently face the adhesive technologist in that some of the best models for understanding adhesion, i.e. Lewis acid/base neutralization reactions, are based on empirical methods. It was thought that computational methods may show a way for addressing this and provide a first principle basis for understanding adhesion.

Current limitations in software, and computer hardware do not yet provide for using computers as a common tool for understanding the adhesive process. HOMO and LUMO values are thought to be directly identified with Lewis acid/base reaction pairs. These values derived using both *ab initio* and semi-empirical methods for a variety of molecules and docked pairs of molecules yield a unreasonably wide ranges of values and thus, are of very limited value. Further work in our understanding of quantum physics and software to deal with large arrays of atoms in a rigorous manner will be needed before computational methods can directly speak to the problems of adhesion science.

14. SUBJECT TERMS

15. NUMBER OF PAGES
12

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT

18. SECURITY CLASSIFICATION OF THIS PAGE

19. SECURITY CLASSIFICATION OF ABSTRACT

20. LIMITATION OF ABSTRACT

The Development of Computational Methods of Adhesion and Adhesive Science and Technology

Final Report

Principle Investigator: William E. Johns
Grant No.: N00014-90-J-1298
Date: July 8, 1992

Introduction

The goal of this research program was to develop a set of computer-based tools to help understanding the adhesive process. To accomplish these tasks, we encountered any number of difficulties. These difficulties were of a hardware/software, personnel, and scientific basis. While we learned a lot about the nature of dealing with the subject of computer-based research in adhesion and adhesives, circumstances worked against our meeting the specifics of the originally defined research proposal.

TASK ONE: *Modify the already existing MACROMODEL program to make it more suitable for adhesion research.*

This task was undertaken with the understanding that we would have the ongoing help from the director of the Macromodel program director, Dr. Clark Still of Columbia. Dr. Still had done all past work within the VAX environment, typically using Evans and Sutherland high resolution monitors, equipment we have available to us. Shortly after the project started, Dr. Still's Laboratory acquired a Silicon Graphics platform. All work on the further development or support of the VAX-based Macromodel stopped with the switch to the UNIX environment. Dr. Still informed us that he was no longer interested in any aspect of VAX-based Macromodel development. Since we did not at that time have access to an SGI on campus, we were out of luck.

Another aspect of this task was the hiring of a post doctorate to do the programming. I quickly learned that post-doc's in computational chemistry are non-existent. I made numerous attempts to find such a person, but to no avail. I did finally find a person with a dual bachelors degree in computer science and biology. This person, a Chinese student, had applied for a position with the VADMS (Visualization and Design in Molecular Systems) Center here at WSU at a technical programmer. He interviewed second out of 9 and was beat out by someone more familiarity with genetics. I felt fortunate to have such a person, but was grossly mislead. This person was more interested in getting a green card and getting married to a national than in the program of research. I had to release him (first time in my professional career I've ever had to release anyone.)

Without the help we had expected form Clark Still's lab and without a full time programmer, we were not able to meet this section of the program.

Task TWO: *Use currently existing computational tools to develop a library of surfaces for general use. Compare existing computational derived energies of adhesion with literature values.*

I had some serious problem with this topic. First, the concept of comparing computational values with values derived from the literature. Energies are calculated in typical molecular mechanics force fields as kJ/mol or kCal/mol. One of the advantages of Macromodel as a research tool is that it provides within the shell, three different commonly used force fields, MM2, AMBER, and OPLS/A. Each force field has a unique method for calculating the internal energy of a system. The energy from one set of calculations bears little resemblance to the energy calculated with another. For instance, propyl alcohol when minimized with MM2 will have an internal energy of 10.22 kJ/mol, AMBER yields 3.01 kJ/mol, and OPLS/A yields -0.01 kJ/mol. This is a seriously wide range of values, and all derived from within Macromodel. To then compare the energies derived from a Macromodel environment with another modeling environment, such as BIOGRAF, or SYBYL quickly became a questionable pursuit. There is no basis for holding one set of values in higher regard than another.

A similar problem existed on a more nuts-and-bolts basis when trying to develop a library of surfaces to use for modeling. Given the problems of different energies from force fields, the mere compatibility of one program's data files with another became a serious point of consideration.

Well into the second year of this project, Boeing Aircraft Comp. made it possible for us to purchase used SGI monitors for a nominal amount. The VADMS laboratory purchased several of these machines and several companies were invited in to our laboratory to demonstrate their software. While some software claimed compatibility with Macromodel, none could actually demonstrate it. Further, the major commercial programs have a difficult time in reading each others data files, not surprising considering the competitive nature of this industry. Everyone was "working" on ways of providing such a compatibility in the future.

TASK THREE: *Development of a force field for computationally deriving adhesion forces.*

While this task was not originally expected to take up a significant portion of the overall projects time, it turned out to be one of the most fruitful and one where significant advances in understanding the adhesive process took place.

There is an understanding that Lewis acid/base or donor/acceptor interactions are somehow very closely identified with the adhesive process. Lee (1, 2) in two book has developed this school of thought. The work of Fowkes (3, 4) points to a direct relationship. In our own work we solved a long-standing mystery of wood-solvent using the donor number (DN) and acceptor numbers (AN) of Gutmann (5). Wood was selected because it is a natural composite, i.e. cellulose bonded together with a polyphenolic material lignin. We were able to explain the interactions of solvents on wood, correlating the MOE, rupture strength and acoustic emission of wood under bending loads, often with r^2 values greater than 0.99 with simple models of donor and acceptor number (6). A particularly strong model correlated strength values of wood against $DN/(mv)^{1/3}$ where mv is the molecular volume of the treating solvent. Since DN are measured in calories or joules, we have energy divided by the cube root of volume, which in the cgs system, is cm. Thus, energy divided by cm is force. We have determined a very strong correlation between the physical reaction of a polymeric solid and a force-related value of the treating solvent.

The general problem with this approach is that the acid/base numbers or donor/acceptor numbers are all derived using empirical methods. There is no first principle way of calculating donor numbers and acceptor numbers. For adhesive researchers this is most frustrating.

We spent a good deal of time focusing in on this problem. Our initial approach was to calculate the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals for molecules and then attempt to determine if we could identify relationships between these values and the donor number and acceptor numbers of Gutmann.

Two approaches were considered. First we were able to get a little time on the super computer platform at Cornell and ran a series of *ab initio* calculations using a variety of basis sets for a variety of solvents. On local computers we did similar runs using MOPAC, a semi-empirical software program.

Table 1 shows the results of a series of runs made with Gaussian 86. Methanol was selected as a target molecule because it is a well studies solvent in Lewis acid-base reactions. Here we see that selection of various basis sets generated energy gaps ranging from 16.340 to 25.368 ev or a difference of 55.25 %. Table 2 shows a set of data for methanol determined with MOPAC. Here we see a closer range of energy gaps, but all values falling below the lowest for methanol determined with Gaussian 86.

A series of docking experiments was conducted using MOPAC. Docking is defined as the minimization of two or more molecules in close proximity, mimicking the adhesive process. Either methanol or urea was docked against graphite modeled with a varying number of unsaturated rings. Table 3 shows a range of 68% for energy gaps of methanol against graphite while Table 4 shows a range of values of 277% for urea against graphite. The energy gaps, related to HOMO and LUMO values and thus theoretically related to acid/base values is very sensitive to the size of the graphite surface used. To explore this phenomenon, a series of runs were made varying the size of the graphite substrate with MOPAC. Table 5 shows that energy gap values vary by as much as 91% for the larger surfaces. Since we were limited by the size of our computer is was not possible to explore significantly larger systems.

The outcome from these computer experiments was a bit frustrating from two points of view. First, we could identify any number of legitimate parameters that would yield most any HOMO and LUMO values desired, i.e. determine the HOMO and LUMO values desired for any molecule, we can tell you how to "legitimately" calculate them. This is a problem with our current understanding of quantum physics and related limitations with software.

Another aspect of this problem was in any attempt to correlate these values with calculations based on molecular mechanics force fields. For example, the reasonable approach was to create a model graphite surface and then dock a molecule such as methanol or urea to it. By determining the total energy, and then the energy of each component, it should be possible to determine the secondary bond energies which are unique to the total assembly which are not present with individual components. Such an experiment using molecular mechanics force field MM2 yield secondary forces between graphite and methanol of -0.0149 ev and graphite and urea of -0.243 ev. These compare within an order of magnitude for some values of the energy gap for similar systems when determined by MOPAC, but not for others. Similarly, MOPAC will agree with some values for the energy gaps for graphite with Gaussian 86 but not others. It is heartening to note that these values, roughly bracket the range of energies thought to be responsible for adhesive systems, 1 ev = 23.06 kCal/mole. The problem remains. There is no obvious way to determine which values more closely represent reality. We are limited by the size of the arrays we can compute and are unable to work with realistically large systems.

The second problem is more fundamental in our understanding of the science involved. Donor numbers as published by Gutmann (3) can be shown to directly correlate with the properties of solid materials and with the joint strengths of adhesive substrate systems. Donor numbers are determined by measuring the heat of interaction of a solvent against a known acid, typically antimony pentachloride. We perceive this to be a reaction of $SbCl_5$ acting like the perfect acceptor and the unknown donating in some measurable fashion, a share in an electron pair. Acceptor numbers are based on shifts within the ^{31}P NMR spectra for triethylphosphine oxide, a standard reference base, dissolved in various solvent. This is how we perceive the reaction. In fact that is not the only thing that is happening to generate heat or induce the NMR shift. In the calorimeter or NMR we have, in addition to this simplistic reaction, a contribution of electrostatic forces, London forces, hydrogen bonding, and other forces all influencing the reaction. Thus:

$$\Delta H_{total} = \Delta H_{acid\text{-}base} + \Delta H_{London} + \Delta H_{electrostatic} + \Delta H_{hydrogen\ bonding} + \Delta H_{other}$$

To date researchers have been trying to computationally derive the energy of acid-base interactions, <u>or</u> dispersive forces <u>or</u> electrostatic interactions and call that value the forces of adhesion. Any real system, something as simple as placing a drop of water on a clean glass slide will in all likelihood involve acid-base neutralization factors, along with dispersive interactions, possibly some chemical bonding, hydrogen bonding, and perhaps even other factors we don't yet know of. Alas, this project has demonstrated to me the immense complexity of defining the forces of adhesion computationally.

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Table 1. GAUSSIAN calculations of methanol (orbital energies)

	Basis sets				
Energy level	STO-3G	3-21G	4-31G	6-31G	6-311G
1	-20.2633	-20.4353	-20.5103	-20.5504	-20.5437
2	-11.0858	-11.2117	-11.2523	-11.2738	-11.2750
3	-1.2785	-1.3346	-1.3515	-1.3544	-1.3576
4	-0.8770	-0.9271	-0.9372	-0.9389	-0.9396
5	-0.6110	-0.6692	-0.6828	-0.6840	-0.6866
6	-0.5713	-0.6139	-0.6217	-0.6218	-0.6230
7	-0.5172	-0.5771	-0.5889	-0.5897	-0.5918
8	-0.4187	-0.4809	-0.4878	-0.4888	-0.4917
9	-0.3594	-0.4345	-0.4446	-0.4456	-0.4479
10	0.5729	0.2661	0.2274	0.2224	0.1526
11	0.6507	0.3158	0.2744	0.2724	0.1844
12	0.6969	0.3452	0.3187	0.3159	0.2232
13	0.7234	0.3554	0.3233	0.3225	0.2303
14	0.7345	0.4245	0.3914	0.3740	0.3325
15	0.9419	0.8503	0.7662	0.4567	
16	0.9623	0.8681	0.7828	0.4812	
17	0.9677	0.8723	0.8014	0.5980	
18	1.2479	1.1415	1.1247	0.6706	
19	1.3147	1.1860	1.1735	0.7316	
E-gap (au)	0.9323	0.7006	0.6720	0.6680	0.6005
E-gap (ev)	25.368	19.063	18.285	18.176	16.340

Table 2. MOPAC calculations of methanol: orbital energies (ev)

Energy Levels	Hamiltonians			
	MINDO/3	MNDO	AM1	PM3
1	-32.0896	-41.9264	-37.8433	-38.1971
2	-24.6268	-27.8236	-26.9845	-26.4865
3	-17.3034	-18.6721	-18.2860	-18.0183
4	-15.2853	-15.3874	-15.4416	-15.5270
5	-14.0382	-15.3171	-15.2892	-15.5051
6	-11.9328	-12.8217	-12.5023	-12.4843
7	-11.0781	-11.4124	-11.1306	-11.1294
8	2.1020	3.7950	3.7758	3.5152
9	3.4907	3.9294	4.0984	3.9023
10	3.7895	4.6937	4.2238	4.2111
11	4.0557	5.0164	4.5217	4.3928
12	5.6273	6.7591	6.2475	5.6422
E-gap (ev)	13.180	15.207	14.906	14.645

Table 3. MOPAC calculations of Graphite docking with methanol

	Heat of formation kCal/mole	Total energy (ev)	HOMO (ev)	LUMO (ev)	E-Gap (ev)
GR1- MNOL	-35.14321	-1359.01051	-9.45010	0.26760	9.718
GR2- MNOL	-16.93320	-1898.19299	-0.09940	0.89581	0.995
GR3- MNOL	-8.94363	-2309.91058	-0.07989	0.47358	0.553
GR4- MNOL	19.69822	-2976.55452	-0.54862	0.02518	0.574
GR5- MNOL	43.72589	-3515.73055	-0.23373	0.10632	0.340
MNOL	-57.35040	-507.51138	-11.41242	3.79504	15.207

MNOL: methanol

GRx: indicates graphite modeled with x number of unsaturated rings.

Table 4. MOPAC calculations of Graphite docking with urea

	Heat of formation kCal/mole	Total energy (ev)	HOMO (ev)	LUMO (ev)	E-gap (ev)
GR1_UREA	-114.76077	-2730.77924	-9.37402	0.36825	9.742
GR2_UREA	-91.84441	-3269.7605	-0.0792	0.92206	1.001
GR3_UREA	-86.71026	-3681.60190	-0.52618	0.07002	0.596
GR4_UREA	-56.92276	-4348.19616	-0.47622	0.07941	0.555
GR5_UREA	-38.37023	-4887.36665	-0.15798	0.20588	0.363
GR6_UREA	-44.74146	-4859.31175	-0.12439	0.16980	0.294
GR7_UREA	-47.13858	-5115.23760	-1.01998	0.08804	1.108
UREA	-138.14460	-1879.33400	-10.70121	1.23721	11.938

GRx: indicates graphite modeled with x number of unsaturated rings.

Table 5. MOPAC/MNDO calculations of graphite with different pseudo-structure size (Input geometries initially MACROMODEL optimized)

	Heat of formation	Total energy	HOMO	LUMO	E-Gap (ev)
GF1	21.32946	-851.53433	-9.39507	0.36667	9.76174
GF2	38.35057	-1390.77122	-0.02527	0.99653	1.02128
GF3	46.58198	-1802.47832	-0.00453	0.56482	0.56935
GF4	60.85625	-2185.59220	-0.39501	0.43306	0.82807
GF5	94.29818	-3008.27012	-0.13583	0.21879	0.35462
GF6	87.86038	-2980.21811	-0.09720	0.19292	0.29012
GF7	110.72839	-3519.20146	-0.31008	0.00106	0.31114
GF8	117.47348	-3774.73088	-0.03482	0.32037	0.35519
GF9	116.19347	-4030.60828	-0.12305	0.4311	0.55420
GF10	140.49706	-4569.52939	-0.19285	0.27947	0.47232
GF11	161.27584	-4824.45026	-0.31068	0.07986	0.39054
GF12	152.89811	-5080.63545	-0.26108	0.02979	0.29087

GF indicated a graphite surface modeled with an indicated number of rings.