

The use of molecular modelling in studying pitch deposition

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SUMMARY

Molecular modelling is proving to be a useful tool in understanding the fundamental interactions between molecules and surfaces. With the use of the super-computer at Australian National University (ANU) calculations on quite large molecules such as triglycerides and polymers can be made. The effect of the chemical structure of different fixatives on the interaction with the various components within pitch can be understood with the use of molecular modelling. Care is needed in choosing the most appropriate method to model the interactions. Geometry optimisation at the higher level of theory using quantum mechanics is needed. Comparison of different quantum mechanical methods yielded similar results indicating that the methods using the less computing power would be adequate in helping to gain a more fundamental understanding of the interactions that occur between various fixatives and pitch.

KEYWORDS

Pitch deposition, molecular modelling, wood extractives, fixatives

INTRODUCTION

Major developments in physical and biological sciences over the past ten to twenty years have been helped by increased computing power and the development of programs to model behaviour of molecules. This rapid developing field of science is called Molecular Modelling. It is also referred to as Computational Chemistry.

In the past molecular modelling and computational chemistry have been the domain of theoretical chemists but more non-theoreticians are now utilising molecular modelling because of the accessibility of high power computers and software

that enable calculations to be made. Increased computing power has allowed scientists to do things that previously were too difficult because of the complexity of the mathematics and the large number of calculations involved. Graphical interfaces make it easier for non-experts to undertake molecular modelling and thus use it to support experimental work. The calculations themselves become an experiment as parameters are varied and the results of the calculations analysed.

Molecular modelling is being used successfully in designing drugs and understanding proteins, DNA, lipids, carbohydrates and enzyme reactions (1-4). It is still a relatively new area in the pulp and paper industry but it is already beginning to make a mark. It has been a tool used by researchers since the 1980's to help understand the reactivity of lignin and to propose bleaching mechanisms (5-9). More recently it has also been used to understand wet end chemistry and the chemical interactions that take place (10-14).

Embarking on molecular modelling can be a daunting task for a non-expert. It is important to have some understanding of the basic theory involved in order to avoid many of the potential pitfalls that might arise (15). When starting out a novice is faced with a large number of acronyms for example HF/STO-3G and B3LYP/6-31G(d), each defining the type of calculation. The user needs to decide what is the best method to apply and more importantly how to determine if the calculated results make sense.

The purpose of this paper is to describe at a basic level what is involved in molecular modelling and what sorts of calculations are possible. The advantages and disadvantages of the different approaches are discussed. The paper presents results of calculations that have been undertaken to support experimental work investigating the interactions between the components of wood pitch and pitch fixatives (16). By understanding how different fixatives interact with different components papermakers and chemical suppliers will be able to better tailor and design reten-

tion aid systems to a particular paper mills requirements.

What is molecular modelling?

In the past molecular modelling would have been considered to be the construction of model molecules using kits of coloured balls representing different atoms and rods representing the bonds between them. These models enabled chemists to visualise the structure of the molecules in three dimensions. By rotating bonds, changing bond lengths etc, the chemist was able to investigate the behaviour of the molecules and the interactions with other molecules. Today this is carried out using computers. Computers have extended applications for which molecular modelling can be used.

There are three main types of calculations, sometimes referred to as the level of theory, used when doing molecular modelling. These are:

1. Molecular mechanics
2. Semi-empirical
3. Ab Initio.

Each method has its own strengths and weaknesses. Thus, research is required to find the best method for a particular theoretical investigation. In evaluating methods computational time and cost are important factors to consider, as higher levels of theory are more expensive in terms of computing time. Table 1 compares quantum mechanics and molecular mechanics.

The calculations involved in molecular mechanics are much simpler than the semi-empirical calculations while the *ab initio* calculations are the more rigorous. As a result the molecular mechanics calculations are faster and the *ab initio* calculations take longer and use more computing power. Molecular mechanics is the method of choice for computing the structures and energies of medium to large molecules (50-100+ atoms).

Molecular mechanics (MM) is an empirical method based on a simple classical-mechanical model of molecular structure (17). MM models molecules as a series of balls and springs. The calculat-

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Table 1
Comparison of Quantum and Molecular Mechanics

Advantages	Molecular Mechanics	Quantum Mechanics
Conceptual simplicity	•	
Speed of computations	•	
Capability to treat large molecules	•	
Inclusion of solvation effects	•	
Conformational analysis of "normal" molecules	•	
Determination of geometries and relative energies	•	
Generality of parameterisation		•
Applicability to short-lived species		•
Treatment of intermediate/unknown hybridisations		•
Determination of electronic properties		•
Theoretical rigor		•

ed energy is the sum of contributions arising from the 'ideal' bond distances, angles, torsional angles and non-bonded contributions such as the van der Waals and charge-charge interactions (18). In the calculations a set of equations, called a force field, is used. The parameters used to define the force fields have been derived experimentally and also by calculation. In calculating the energy of any system only the nuclei positions are considered and the electrons are included implicitly. This can lead to inaccuracies as molecular orbital interactions are unaccounted for (19). This method has the advantage that more atoms can be included in the calculations compared with higher levels of theory (18,19). Some commonly used force fields are AMBER, CHARMM, MM2 and MM3. AMBER and CHARMM have been constructed for biological molecules and are not really suitable for assessing geometries of sterically congested molecules (15). MM2 and MM3 were developed for aliphatic alkanes (20).

Semi-empirical and *ab initio* methods calculate the energy of a molecule by considering the interaction of each electron with the average field of all the other electrons. Quantum mechanics gives a mathematical description of the behaviour of electrons using wave functions (21). Account is taken of the kinetic energy of the particles and Coulombic interactions between the electron and nuclei. Semi-empirical methods simplify the calculation by neglecting core orbitals. These methods are based on quantum mechanics, but also include values obtained through empirical parameterization (22).

Ab initio calculations only use mathematical approximations called basis sets to calculate the atomic and molecular orbitals, thereby removing experimental

bias, and can be applied to systems where experimental data is not available. The calculations are more complex and require more computing time than for MM (21). The most common type of *ab initio* calculation is the Hartree Fock (HF) calculation. An alternative to the *ab initio* method is Density Functional Theory (DFT) which looks at the total electron density rather than a wavefunction to calculate the energy of a molecule (23).

What is involved in doing the calculations?

After deciding what calculations are required the user must provide some starting information. This input generally contains three parts:

- The geometry of the molecule which includes either a set of cartesian coordinates or a list of atom types, bond lengths, bond angles and dihedral angles. This geometry is just a starting point created using a computer package that defines the appropriate bond lengths and angles.
- The kind of calculation to be done eg single point energy calculation or optimised geometry calculation to find the minimum energy conformation
- The starting set of mathematics and approximations given by a command that indicates the method being used and the basis set. For example the command line HF/6-31G(d) indicates that Hartree Fock approximation will be used using a basis set of 6-31G(d).

The basis set is a table a numbers which mathematically estimates where the electrons might be. There are different basis sets depending on the degree of accuracy required. However, the greater the degree of accuracy of the basis set the larger the calculation.

Solvation

The molecular mechanics and molecular orbital calculations treat the molecules as being alone in a vacuum. There are no neighbouring molecules of any kind and also no solvent. For many applications the gas phase calculations adequately model and predict the information required. For other systems where molecules are in solution and solvent-solute interactions are important then it may be important to model the systems in the presence of solvent molecules. The interaction between the solvent and solute molecules may have a significant effect on the way the molecules in the complex interact. The simplest way to take into account the influence of the solvent is to include the appropriate dielectric constant. This assumes that the major effect of the solvent is to screen the electrostatic interactions of the solute (1). This method has clear limitations as it does not consider solvent-solute interactions.

Another method used to account for solvation is to construct a solvent shell consisting of anywhere from several dozen to several hundred solvent molecules about the solute. The size of the system usually prohibits analysis by quantum mechanical methods.

The third approach is to treat the solvent as a continuum which is characterised by a bulk dielectric constant. The solute molecule is placed in a cavity in the solvent. In the calculations the surface of the cavity is divided into small tesserae. The free energy of solvation is determined and is equal to the free energy change to transfer a molecule from vacuum to solvent. The main contributions to the solvation come from:

1. The cavitation energy of the formation of the hole which preserves the dissolved species in the solvent
2. The electrostatic interaction of the solute with the solvent
3. The dispersion and repulsion energies

The third approach is the one undertaken in this paper. The results of including solvation are compared with the gas phase calculations in order to determine the best approach to model the pitch-fixative interactions. It is very easy to generate numbers from the calculations and also create 3-D models on the computer screen but to ensure they are meaningful they need to have some basis in the experimental work.

EXPERIMENTAL

Laboratory studies of deposition behaviour of model pitch dispersions and various polymeric fixatives have been previously reported and the experimental procedure described (16).

Theoretical Calculations

The chemical structures of the resin acids, fatty acids, triglycerides and model structures for the fixatives investigated were first drawn in Spartan[®]. Initial geometry optimisation of each molecule and then the complex formed between the wood extractives and the model polymeric fixatives was carried out using molecular mechanics and the MM3 force field on the Pentium cluster of fifteen dual processor Pentiums using a Linux operating system at School of Chemistry University of Tasmania. Further optimisation of the geometry was undertaken using *ab initio* calculations through the supercomputer at the Australian Partnership for Advanced Computing (APAC) facility in Canberra using the Gaussian 03 program. Both Hartree Fock and density functional theory were used with a variety of basis sets.

The heat of formation (H_f) for each single component and interaction was obtained via the Gaussian 03 program using Hartree Fock and density functional theory. The minimum basis set STO-3G as well as the split-valence basis set 6-31G(d) which added a set of *d* polarisation functions to each heavy atom were used.

Solvation Free Energy (ΔG_{sol}) for the individual molecules and also complexes were determined using the polarisable continuum model with both HF and DFT levels of theory using Gaussian 03 program on the APAC super computer.

RESULTS AND DISCUSSION

A series of laboratory experiments had been undertaken and previously reported (16) to investigate the interaction between various polymeric fixatives and wood resin extractives that lead to pitch formation. In this study model compounds of abietic acid, oleic acid and triolein were used to represent the major components of wood resin extractives. The fixatives investigated were polyethyleneimine (PEI), cationic polyacrylamide (CPAM), a medium and a high charged co-polymer of polyacrylamide and poly (diallyldimethyl ammonium chloride) (denoted by MCD PAMDAD and HCD PAM-

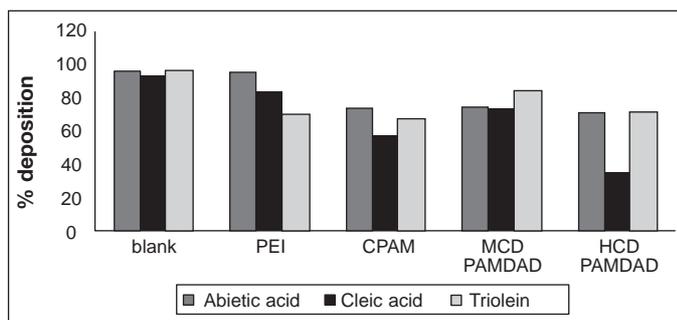


Fig. 1 Deposition of abietic acid, oleic acid and triolein in the absence of fibres at pH 7.

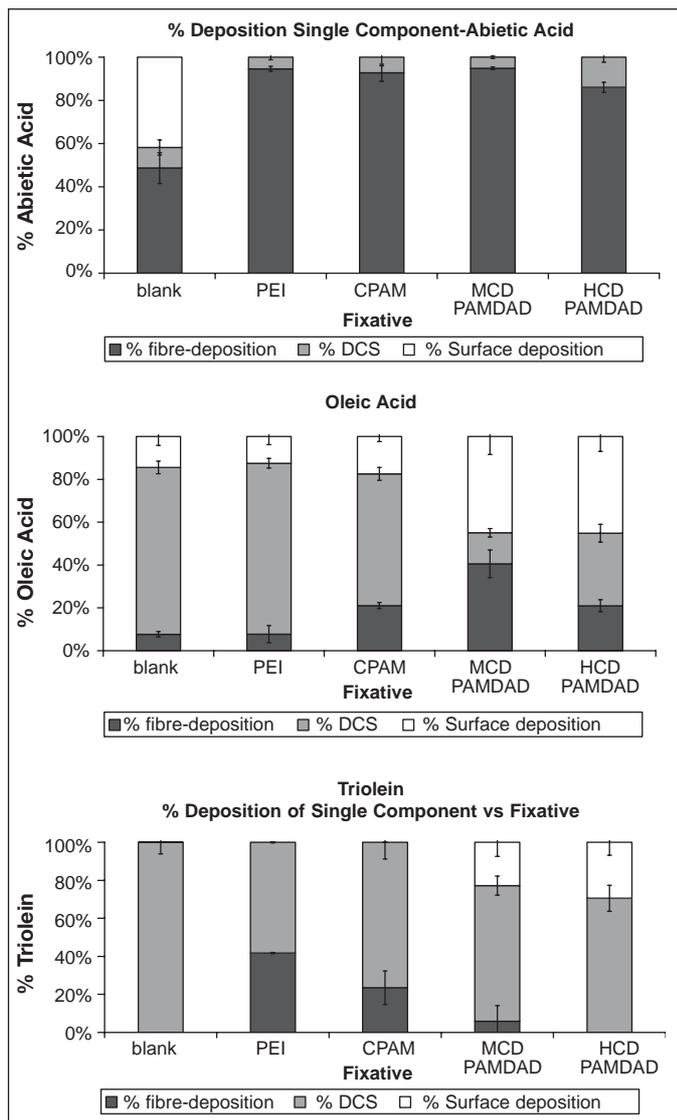


Fig. 2 Deposition of abietic acid, oleic acid and triolein in the presence of fibres at pH 7 (Error bars indicate ± 1 std.dev. from mean).

DAD). The results of the experiments in which each of the four different fixatives were added to the individual model components at pH7 in the absence and presence of fibres are shown in Figures 1 and 2. In the absence of fibres (Fig. 1) abietic acid, oleic acid and triolein show a strong deposition tendency. The addition of the fixatives appears to reduce this deposition

tendency indicating that an interaction between the fixative and wood resin component is occurring. The results indicate that slight differences in the fixative - wood resin interaction occurs between the various fixatives, with CPAM and the two copolymers reducing the deposition tendency of abietic acid to a greater extent than PEI while PEI and CPAM reduce

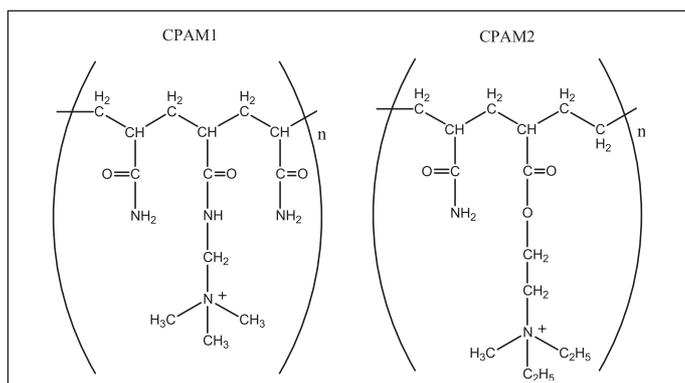


Fig. 3 The monomers of CPAM-1 (left) and CPAM-2 (right)

oleic acid deposition and the high charged copolymer reduces triolein deposition.

In the presence of fibres (Fig. 2) all the fixatives appear to selectively attach abietic acid onto fibres at 1 kg/tonne addition. Oleic acid, on the other hand, appears to be stabilised in the dissolved colloidal fraction in the absence of fixative and the addition of PEI was found to have very little impact. The addition of CPAM and the copolymers appear to reduce the amount of oleic acid in the colloidal phase and deposit it onto fibres and other surfaces. The medium charge copolymer exhibited greater preference in fibre-attachment of the oleic acid. Polyethylenimine (PEI) was found to preferentially interact with triolein.

To further understand the results of the deposition work and gain a better understanding of how the different fixatives interact with wood resin components some molecular modelling calculations were then undertaken. Abietic acid and oleic acid were modelled as deprotonated species in order to investigate the interactions between the charged species under neutral pH conditions. At neutral pH most of the species present would be negatively charged and hence they would interact with positively charged fixatives. Triolein is a neutral species and was modelled as such. Models of the fixatives were constructed by combining several monomers together. The oligomers were only a representation of the fixatives as the molecular weights of the polymers were very large. The end group of the oligomers were also "capped" with a $-\text{CH}_2\text{CH}_3$ functionality to prevent interaction with the end group.

Literature searching provided several possible structures for cationic polyacrylamide (24,25). These tended to differ in groups attached to the cationic nitrogen ($-\text{CH}_3$, $-\text{C}_2\text{H}_5$) and structure of the major

branching chain. Two different types of CPAM as shown in Figure 3 were thus modelled in order to investigate the effect of the chemical structure on the interaction.

Different structures of PEI were also modelled as PEI can have primary, secondary and tertiary cationic nitrogens in its structure (Fig. 4). It is generally thought that the number of primary and tertiary amine groups is equal and amount to 25% of the total amines present, making 50% secondary amines (26).

The stabilisation energy was calculated at different levels of theories and using different basis sets. The stabilisation energy (SE) was calculated to gain an understanding of the stability of the complexes formed. The SE is calculated from the change in H_f between the single components and the complex formed between the two components.

$$SE = (H_fA + H_fB) - H_f\text{complex}$$

If there is a strong stabilisation energy this indicates that the complex has a lower energy than the single components, and therefore is more likely to be formed. A strong stabilisation energy therefore would result in the polymer binding to the component and increasing deposition tendency.

The calculations performed in the gas phase predict that some differences in the interaction between the different fixatives

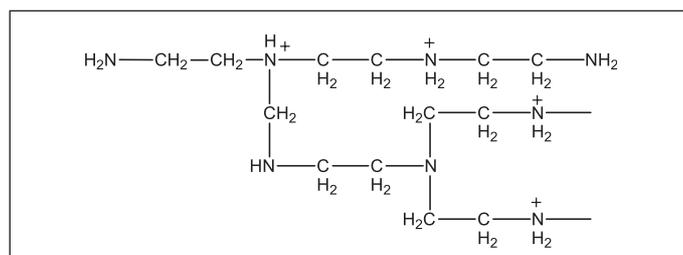


Fig. 4 Typical structure of polyethylenimine

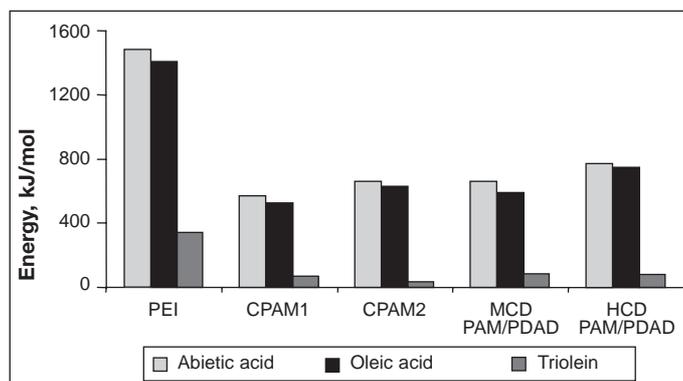


Fig. 5 Comparison of the stabilisation energy for different fixatives and wood extractive components. (B3lyp/6-31G(d) single point energy calculation with MM3 geometry optimisation).

and the wood extractives occur. The methods employed show a strong dependence on the charge-charge interactions between the fixative and the wood resin extractive components. PEI at the same charge density is predicted to form the strongest interaction followed by the copolymers (Fig. 5) though the differences calculated are much more than the experimental deposition results would suggest (16).

What is the best method to use?

The method used to calculate the stabilisation energy particularly for PEI appears to be important as shown in Figure 6. In this figure the results at three different levels of theory are compared for the interaction between primary, secondary and tertiary PEI with abietic acid, oleic acid and triolein. The optimisation of the geometry at the lowest level of theory (MM3) followed by single point calculation of the energy at a higher level of theory using density function theory results in lower values of the stabilisation energy and also some negative values compared to when the geometry is reoptimised at a higher level of theory. Experimental deposition results showed that a complex is formed with triolein (16) and so the negative results indicate that the way the calculations are performed does not prop-

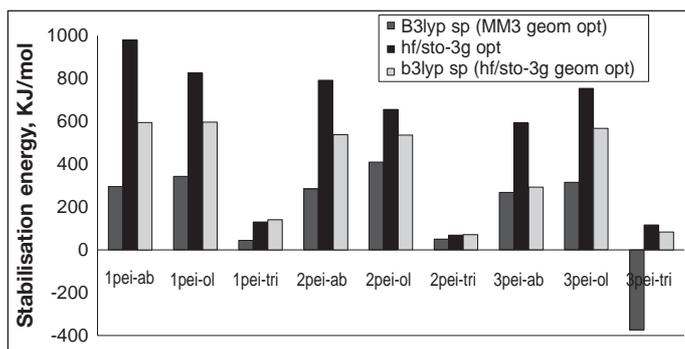


Fig. 6 Comparison of the stabilisation energy for the complexes formed between PEI and wood extractive components. (key: 1pei-ab=primary PEI with abietic acid, 2pei-ol = secondary PEI with oleic acid, 3pei-tri = tertiary PEI with triolein, etc)

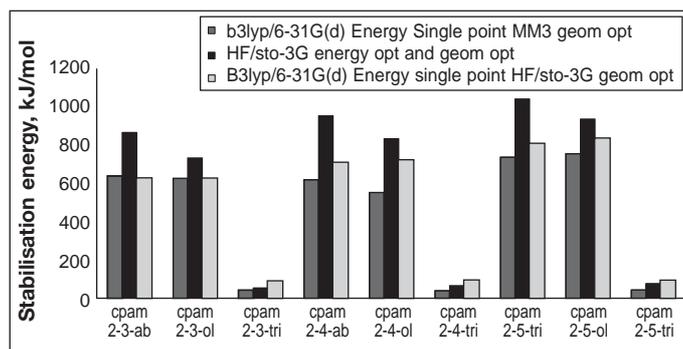


Fig. 7 Comparison of the stabilisation energy for the complexes formed between CPAM (1) and wood extractive components at different charge densities. (Cpam2-3 denotes 3 charges on cpam2; cpam2-4 denotes 4 charges on cpam2 etc.)

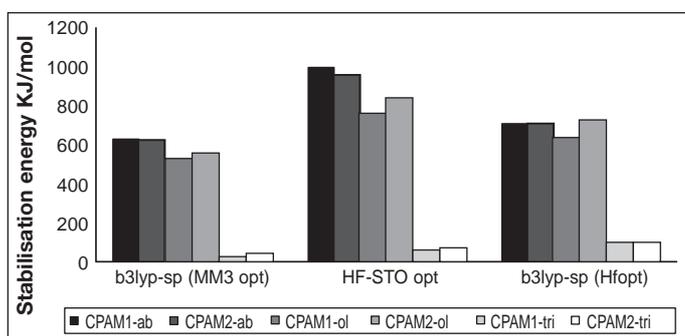


Fig. 8 Comparison of the stabilisation energy for two different CPAM structures with wood extractive components at different levels of theory.

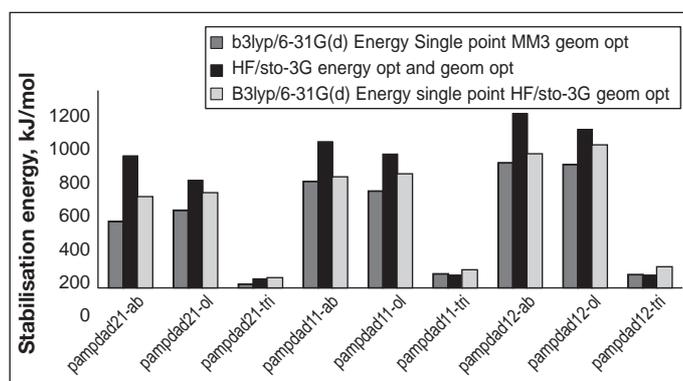


Fig. 9 Comparison of the stabilisation energy for different co-polymer structures and wood extractive components.

erly represent the real system. Re-optimisation of the geometry using *ab initio* methods (HF/STO-3G) appears to overcome this problem and a positive stabilisation energy is obtained for the interaction with triolein though it is significantly lower than the interaction with abietic and oleic acid. This is due to the strong charge interaction between the cationic amine group of PEI and the deprotonated carboxylic acid groups of abietic acid and oleic acid.

The Hartree Fock (HF/STO-3G) calculations predict that abietic acid interacts with primary amine and secondary amine groups in PEI more strongly than oleic acid and that oleic acid interacts more strongly with a tertiary amine group. Slightly different predictions are obtained from the density functional theory (B3LYP/6-31G(d)) calculations which indicate that the stabilisation energy of the complexes with a primary and secondary amine are similar.

What is the effect of charge and chemical structure?

One of the main benefits of molecular modelling is to be able to investigate the effect of modifying the chemical structure

of a fixative and determining the effect this may have on the interaction with the other chemical components.

Interaction with PEI

Calculations of the stabilisation energy show that the type of cationic amine in the PEI affects the strength of interaction with abietic acid as well as oleic acid (Fig. 6). A primary amine forms the most stable complex while the tertiary amine forms the weakest complex. Steric effects appear to be contributing to this.

Interaction with CPAM

The stabilisation energy calculated for the interaction between CPAM-2 and abietic acid, oleic acid and triolein is shown in Figure 7. The CPAM was modelled with three, four and five charges (CPAM2-3, CPAM2-4, CPAM2-5). HF/STO-3G again appears to calculate higher results for the stabilisations of the complexes. Increasing the charge on the fixative was found to increase the stabilisation energy with oleic acid and abietic acid using the three different calculation methods. Varying the structure of the CPAM was found to have very little effect on the sta-

bilisation energy calculated (Fig. 8) for the interaction with abietic acid and triolein though some difference was observed when interacting with oleic acid particularly when the geometry of the complexes were optimised at the higher levels of theory.

Interaction with copolymer

In order to investigate the relative stabilities of differently charged co-polymers, a high, medium and low charged model copolymer were investigated. The model of a low charged polymer was made from a 2:1 ratio of neutral PAM:charged polyDADMAL. The medium charged was a 1:1 ratio of the two monomer groups. The highly charged co-polymer was an oligomer comprising a 1:2 ratio. In order to maintain consistency, the oligomers each comprised six monomer groups. Computational calculations (Fig. 9) predicted an increase in the complex stability with abietic acid and oleic acid as the charge ratio of the charged copolymer increased. This is due to the charge-charge interactions influencing the stabilisation energy. As charge increases, Coulombic attraction would increase and

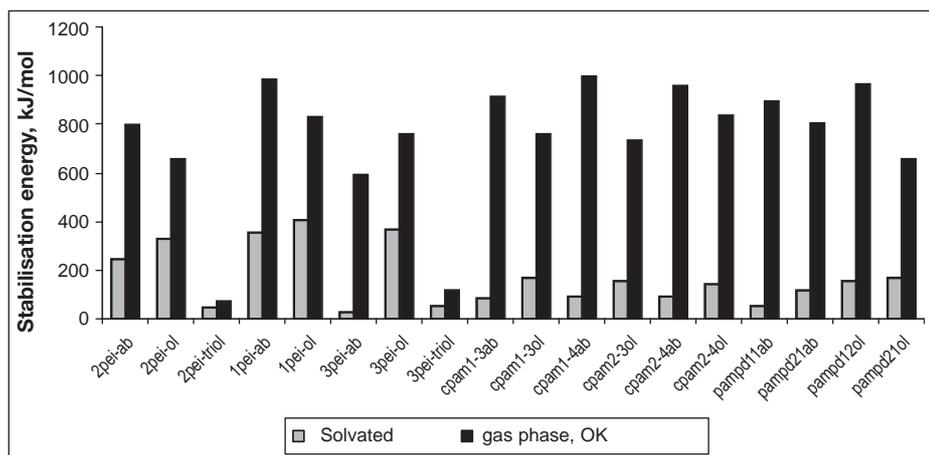


Fig. 10 The effect of solvation on stabilisation energy for different fixative and wood extractive components.

affect the complex energy. Little difference was predicted for complexes with triolein, as the complex only involved charge-neutral interactions.

Effect of Solvation

Calculations were performed to calculate the free energy of solvation and the solvated stabilisation energy. Including solvation does result in a substantial percentage increase in the computation time and memory requirements. Single point calculations in the solvent using the optimised gas phase molecular structure were undertaken. Calculations of the larger complexes with triolein could not be performed because of memory limitations.

Figure 10 shows the calculated stabilisation energy of the interaction between the fixatives studied (PEI, two types of CPAM and a PAM/polyDADMAC copolymer and abietic acid, oleic acid and triolein). The results show that including solvation effects dramatically reduces the calculated stabilisation energy. The decrease in the strength of interaction between the fixative and abietic acid and oleic acid is due to the strong solvent-solute interactions between the individual components and water. A greater decrease appears to occur with the abietic acid compared to the oleic acid. The solvent effects also appear to decrease the interaction with the CPAM and copolymers fixatives compared to PEI. Despite this stable complexes are formed.

There does not appear to be a direct correlation with the deposition results in Figures 1 and 2 and the theoretical calculations of the stabilisation energy of the complexes formed. The calculations indicate a stronger interaction with PEI and the three wood resin components com-

pared to the other fixatives. This is not reflected in the deposition results except for the triolein. There may be several reasons for this. The first being that the calculations were performed on models of the fixatives consisting of only 6 monomer units when in reality there is considerably more. The interaction may be occurring but a complex is formed that is stabilised in the colloidal fraction and not attached to the fibres or deposited.

CONCLUSIONS

Molecular modelling is a powerful technique for helping to understand the interactions between molecules. As computing power increases and as more people become familiar with molecular modelling techniques it will become a powerful tool for papermakers and chemical suppliers.

Care is needed, however, in choosing the correct approach for calculations. It is important that some check be made to ensure that the approach undertaken is valid such as comparing the predicted results with experimental data.

Modelling the effect of the charge and chemical structure of different fixatives provides insight into the parameters and interactions that are important. Calculations show that PEI interacts more strongly with abietic and oleic acid than CPAM and PAM/poly DADMAC copolymers. Increasing the charge on the polymer increased the interaction and the type of cationic nitrogen was also important.

For the purpose of the fixative-pitch systems being modelled it was found that optimising the geometry at the lowest level of theory and then a single point calculation of the energy at a higher level of theory seemed adequate for modelling the interactions with abietic acid and oleic acid. This

approach was not appropriate for the triolein complexes as negative stabilisation energies were obtained. Reoptimisation of the geometry at the higher level of theory (Hartree Fock) with a minimum basis set (STO-3G) was needed.

Including the effect of solvation greatly increases the computing time and memory required. Some of the larger triolein complexes could not be calculated using ab initio methods. The calculated values show that the strength of interaction between the solute molecules decreases due to strong solvent-solute interactions compared to gas phase calculations. Differences in the trends between the solvation calculations and the gas phase calculations were evident indicating that it is important to include solvation when predicting trends in interactions between fixatives and wood extractive components.

ACKNOWLEDGEMENTS

Financial support for this project was provided by Norske-Skog Paper and an ARC Linkage grant. Computing time on the Super Computer at the Australian Partnership for Advanced Computing National Facility was obtained through the Merit Allocation Scheme.

Lynsey Maher is acknowledged for carrying out the MM3 geometry optimisation and energy calculations at B3LYP/6-31G(d). The assistance and advice from the computational chemistry group in the School of Chemistry, University of Tasmania was greatly appreciated.

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Original manuscript received 1 August 2006, revision accepted 4 September 2007