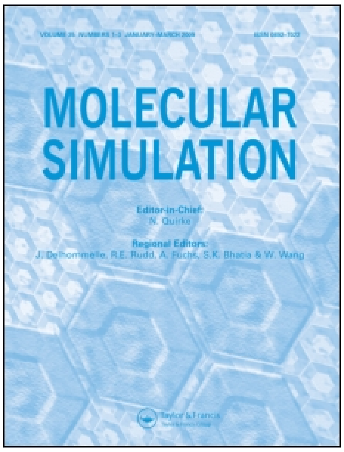

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

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Tom A. Kavassalis[a]; Phillip Choi[b]; Alfred Rudin[b]
[a] Xerox Research Centre of Canada 2660 Speakman Drive Mississauga, Ontario, Canada [b] Department of Chemistry, University of Waterloo Waterloo, Ontario, Canada

To cite this Article Kavassalis, Tom A. , Choi, Phillip and Rudin, Alfred(1993) 'The Calculation of 3D Solubility Parameters Using Molecular Models', Molecular Simulation, 11: 2, 229 — 241
To link to this Article: DOI: 10.1080/08927029308022510
URL: http://dx.doi.org/10.1080/08927029308022510

Molecular Simulation, 1993, Vol. 11(2-4), pp. 229-241
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THE CALCULATION OF 3D SOLUBILITY PARAMETERS USING MOLECULAR MODELS

TOM A. KAVASSALIS[1], PHILLIP CHOI[2] and ALFRED RUDIN[2]

[1]Xerox Research Centre of Canada 2660 Speakman Drive Mississauga, Ontario Canada L5K 2L1

[2]Department of Chemistry University of Waterloo Waterloo, Ontario Canada N2L 3G1

(Received December 1992, accepted April 1993)

In this paper we describe the use of molecular mechanics models to examine detailed intermolecular interactions within the liquid state of a common nonionic surfactant system, nonyl phenol ethoxylate (NPE). Using constant energy molecular dynamics simulations we have studied the relative strengths of dispersive interactions versus polar interactions and have estimated three dimensional solubility parameters for NPE systems as a function of temperature and ethylene oxide content. The predictions at 300 K are in good agreement with three dimensional solubility parameters predicted using group contribution tables. Models of the amorphous liquid state were represented by single molecular structures of NPE in a periodic cell. The solubility parameters predicted with these models were in good agreement with those values derived from models having eight NPE molecules packed into a cell with the exception of the electrostatic interactions, which are the most sensitive to system size effects.

KEY WORDS: Solubility parameters, surfactants, Nonyl Phenol Ethoxylate

1 INTRODUCTION

Nonionic surfactants are widely used in a variety of industrial applications ranging from additives for drilling muds to emulsifiers in polymerization reactions and components of pharmaceutical and cosmetic preparations. They are also widely used for non-industrial purposes such as in household detergents. The solubility properties of nonionic surfactants have been the subject of numerous studies and are reviewed in references (1) and (2). Perhaps the most interesting aspects of the solution properties of theses materials is the rich phase behavior that has been observed for mixtures of water, alkane and nonionic surfactants as well as the practical applications of such mixtures. More often than not, nonionic surfactants are used in many component systems where the phase behavior has not been fully explored.

One of the practical advantages of nonionic surfactants, over their ionic counterparts, is the ability to tailor the polarity of the surfactant by controlling the architecture, composition and temperature. Another advantage of this class of surfactant, is the insensitivity to pH of its solution properties.

The purpose of the study described in this paper is to investigate the role of composition and temperature on the solubility properties of a popular family of nonionic surfactants using molecular level models and molecular dynamics simulations. Our aim is develop and test a molecular simulation methodology that can be used to select surfactants for specific applications and ultimately to design surfactants with properties optimized for particular needs. We essentially construct models with atomic level complexity, simulate these models subject to thermodynamic constraints and then analyze, at the atomic level, the interactions between the surfactant molecules. In particular we look at the nature and strength of various intermolecular interactions.

Solubility properties of nonionic surfactants and even solvents are often expressed in terms of HLB numbers. HLB (hydrophilelipophile balance) numbers were first derived from empirical considerations by Griffin (3,4) in the late 1940s. In the HLB scale, the least hydrophilic materials have low HLB numbers while the most hydrophilic materials have a high HLB number. The HLB scale serves to rank materials with similar properties with a similar number, hence functions as a quantification of the chemists rule of thumb that *like dissolves like* . . .

A more fundamental measure of solubility properties was introduced by Hildebrand and Scott. (5) in the 1960s and later generalized by Hansen (6). In Hansen's approach, the cohesive energy of a material E_{coh}, which measures the strength of internal cohesive forces, is decomposed into contributions from dispersion forces, electrostatic forces and hydrogen bonds. In this way, two materials with similar intermolecular interactions will have similar solubility parameters. Three dimensional solubility parameters were defined by Hansen with the equation

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{1}$$

where the subscripts *d, p,* and *h* refer to dispersion, polar and hydrogen bonding respectively and the overall solubility parameter δ is defined as $\delta^2 = (E_{coh}/V)^{1/2}$. E_{coh} here is defined as the energy change upon isothermal vaporization of the saturated liquid to the ideal gas state and V is the molar volume. The ratio of (E_{coh}/V) is often referred to as the cohesive energy density. The three dimensional solubility parameters are defined by decomposing the cohesive energy into its components arising from dispersive, polar and hydrogen bonding interactions respectively.

The three dimensional solubility parameter has intuitive appeal, but the direct measurement of these parameters is not possible. Even the overall solubility parameter δ is often difficult to measure. In general, indirect methods are used to estimate these parameters which are based in part on statistics. The most popular methods are the so called group contribution methods. Group contribution methods essentially assume that each substructure within a molecule, such as a methyl group, hydroxyl group etc., contributes a certain average amount to the cohesive energy density of a material. By totaling up the various contributions from the component groups of a molecule one obtains a statistical guess as to the overall cohesive energy of a particular material. The underlying fundamental assumption here is the cohesive energy is an additive function of many short ranged interactions that do not depend very sensitively on the architecture of the molecule.

While the group additivity approach may be useful in providing some qualitative guidance, it suffers from the problem that the detailed chemical structure of the molecule, intermolecular correlations and directional polar and hydrogen bonding interactions cannot be taken into account in a satisfactory manner. This becomes particularly important for several classes of surfactants such as the derivatives of cellulose, where the architecture can be quite variable and the hydrogen bonding interaction, which is geometry specific, may dominate the intermolecular forces.

One of the new promising approaches to examining solubility of surfactants builds on the recent work on polymer solubility by Theodorou and Suter (7) using atomistic models. Theodorou and Suter constructed detailed models of amorphous polypropylene from which they estimated the cohesive energy. The atomic level models contained the force field elements necessary to describe the bonding in the molecule as well as the non-bonded inter- and intra-molecular interactions. More recently, the same technique has been extended to a number of other polymers by various other researchers.

In earlier work (8) we extended this method to compute the three dimensional solubility parameters of a common short chain nonyl-phenol-ethoxylate (C_9H_{19}-Ph-$(OCH_2$-$CH_2)_4$-OH hereafter referred to as NPE-4. Using molecular dynamics simulations we were able to anneal our molecular ensembles and study the effect of temperature on the solubility properties. In the present study we extend this work to address a number of issues. First, we examine the basic assumption in our method that a representative model of the bulk amorphous system can be achieved with an ensemble of single molecule conformations using a special periodic boundary condition. This assumption is tested by building models composed of single chains and of many chains and comparing the solubility parameters computed. We then apply the technique to examine the effect of ethylene oxide content on the three dimensional solubility parameters. Next, we examine the effect of temperature on the three dimensional solubility parameters in order to test the equivalence between ethylene oxide content and temperature that is reported in the literature (1). In section 2 we review the force field used in our model and the simulation methodology. In section 3 we compare the results from single chain models to multichain models and we present the results of a composition study and temperature study. In section 4 we summarize the basic elements of the paper.

2 SIMULATION DETAILS

Force Field

In this section we review the details of our simulation with sufficient detail so that the simulation methodology can be applied to other systems. All models used in this work are of the molecular mechanics variety in that the structure and the dynamics of the molecules is governed by a classical force field. Our main interest here is in examining the relative strengths of various nonbonded interactions and the effect of temperature on those interactions. We therefore feel justified in adopting relatively simple parameterizations to describe bonding in the molecules. For our purposes we have chosen the Dreiding force field that is incorporated in the POLYGRAF code (9) and was published recently by Mayo, Olafson and Goddard (10).

The force field potential energy function, U, that we used consists of a sum of seven terms

$$U = U_b + U_\theta + U_\phi + U_{\text{inv}} + U_{\text{vdw}} + U_{\text{el}} + U_{\text{hb}} \tag{2}$$

where the individual terms represent; U_b bond stretching, U_θ bond angle bending, U_ϕ torsion angle rotations, U_{inv} tetrahedral center inversions, U_{vdw} van der Waals or dispersive interactions, U_{el} electrostatic interactions and U_{hb} hydrogen bonding interactions. The first four terms parameterize the short ranged intramolecular interactions that determine the bond lengths, bond angles, etc. The last three terms are nonbonded interactions and can be both intramolecular and intermolecular. For the purposes of predicting solubility parameters the nonbonded intermolecular interactions will be the most important. The Dreiding force field that we selected for this study is described in full detail in reference (10). Our description of the nonbonded interactions will therefore be brief.

Nonbonded interactions are computed between pairs of atoms that are from different molecules (intermolecular) and between atoms from the same molecule (intramolecular) if the atoms are separated by three or more bonds. Shorter ranged intramolecular interactions are implicit in the bonding interaction terms. The Dreiding force field uses a Lennard-Jones (6–12) potential to represent the van der Waals or dispersive interactions.

Electrostatic interactions are modeled by pairwise additive interactions between point charges located at the atomic centers. These electrostatic interactions are very long ranged and depend sensitively on the values of the point charges used. The choice of partial atomic point charges is a subject of some controversy and represents one of the weakest points in the application of molecular mechanics models today. In our calculations we used charge values computed using the charge equilibration (Q-Eq) method that has been published recently by Rappe and Goddard (11).

The Q-Eq method was selected by comparing the point charge values predicted by three empirical methods (9) (Gasteiger, Del Re, and Q-Eq) against charge values derived from Hartree-Fock wavefunctions using the 6–31G level basis set and a Mulliken partitioning scheme (12). A small molecule analog of the NPE-x system, comprised of 26 atoms, was used for this comparison. The structure of this molecule is shown in Figure 1 and the computed partial atomic charges are displayed in Table I. The numbers tabulated in the HF/6-31G column were computed with a fixed nuclear geometry derived from an energy minimized structure without any electrostatic interactions. The Q-Eq method, which is based in part on experimental values of ionization potentials and electronegativities, came closest to matching the Hartree-Fock results, particularly for the two oxygen atoms which according to all of the methods employed in this comparison would have the largest partial charges.

Hydrogen bonding interactions are modeled by a special Lennard-Jones 12–10 interaction that explicitly includes an angular dependence of $\cos^2(\theta_{AHD})$ on the relative geometry of the acceptor A, the hydrogen atom H and the donor D. In our models, the terminal hydroxyl group H atom is the only H atom involved in hydrogen bonding. All oxygen atoms can serve as hydrogen bonding acceptors.

Liquid State Models

The NPE family of surfactants is non crystalline in the liquid state. We have therefore chosen to model these systems using the methodologies developed in recent years by Theodorou and Suter (7) for modeling amorphous polymers to model the liquid state of these materials as well. Theodorou and Suter modeled the amorphous state of polymers such as polypropylene, by using single chain conformations grown within a periodic box. The periodic boundary condition of

Table I Partial atomic charges for molecules depicted in Figure 1 as computed using several empirical methods and a Hartree-Fock calculation using the 6-31G level basis set of Gaussian 90 (12).

Atom Number	*Atom Type*	*Gasteiger*	*Del Re*	*Q-Eq*	*HF/6-31G*
1	C	−0.02	−0.02	−0.07	−0.20
2	H	0.03	0.07	0.13	0.19
3	C	0.12	0.13	0.31	0.43
4	C	−0.06	−0.03	−0.14	−0.18
5	C	−0.02	−0.02	−0.11	−0.22
6	C	−0.05	−0.02	0.04	0.00
7	H	0.06	0.03	0.11	0.19
8	O	−0.49	−0.29	−0.61	−0.84
9	H	0.07	0.03	0.09	0.19
10	C	−0.06	−0.03	−0.12	−0.18
11	C	−0.03	−0.08	−0.26	−0.35
12	C	0.11	0.03	0.07	0.06
13	H	0.06	0.03	0.11	0.19
14	H	0.03	0.04	0.13	0.17
15	H	0.03	0.04	0.14	0.16
16	C	−0.06	−0.12	−0.42	−0.44
17	H	0.07	0.05	0.14	0.17
18	H	0.07	0.05	0.14	0.17
19	C	0.08	0.05	0.00	0.01
20	H	0.02	0.04	0.15	0.15
21	H	0.02	0.04	0.14	0.16
22	H	0.02	0.04	0.14	0.15
23	H	0.06	0.05	0.14	0.17
24	H	0.06	0.05	0.14	0.17
25	O	−0.39	−0.46	−0.71	−0.74
26	H	0.21	0.03	0.33	0.41

the unit cell is used in this case to form a space filling structure from a single chain conformation. The presence of periodic replicates of the parent chain provides a very simple and elegant way to introduce intermolecular interactions without increasing the number of atoms needed to represent the solid or liquid state.

The approximation that the single chain model introduces is believed to be negligible provided that the polymer was of sufficient length. The length required would be determined by the flexibility of the polymer. For the NPE-x family of surfactants where we are interested in systems with small chain length, the validity of the single chain representation needed to be tested. In order to test this approximation, we constructed models of the liquid state with single chains and with eight distinct chains (See Figure 2). In both cases the models were constructed with the prescription described below.

Molecular dynamics simulations for systems with large numbers of atoms typically require days or weeks to perform even on current high end workstations. Consequently, only the picosecond to a few nanosecond simulation regime is accessible by this technique. Unfortunately this is insufficient time for many systems such as polymers in the condensed state, to undergo very drastic reorientation and relaxation. It is therefore imperative that the initial state of the system be as close to representing an equilibrated state as possible. In our simulations we have made the widely used assumption that the distribution of conformational features, such

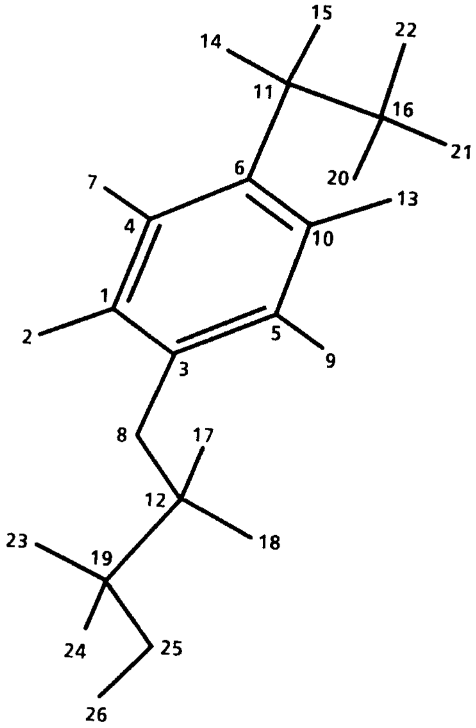

Figure 1 Small molecule analog of the NPE system used in the calculation of partial atomic electrostatic charges. The labels here refer to the atom numbers in Table I.

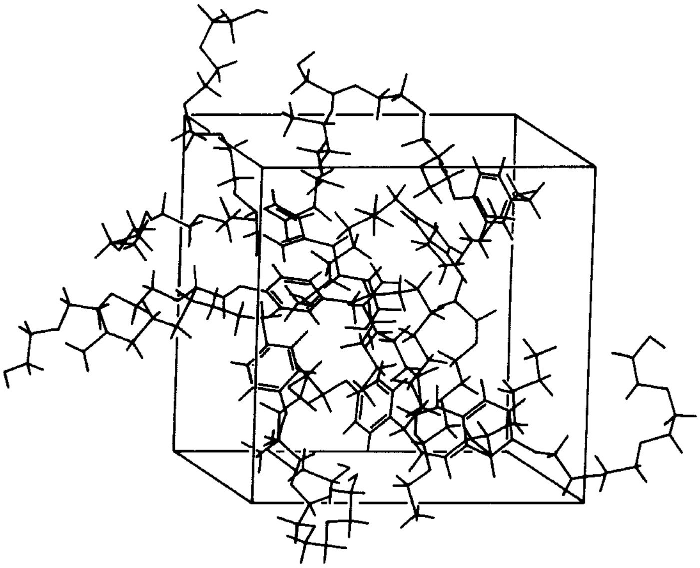

Figure 2 Model of the condensed state of NPE-4 represented by eight NPE-4 molecules in a periodic cell. The intermolecular energy of packing these molecules in the unit cell is used to compute the 3D solubility parameters.

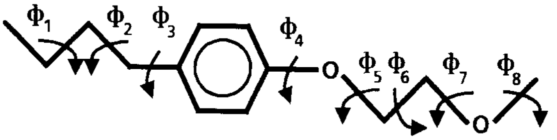

Figure 3 Segment of the NPE-x structure with eight unique torsion angles labeled. A conformational analysis of each of these independent torsion angles was used to prepare the initial state of the NPE-x amorphous systems.

as torsion angles, in the bulk amorphous structure, are the same as those of an isolated molecule. i.e., the molecular conformations in the bulk are unperturbed by the nonbonded intermolecular interactions. This will clearly not be the case for systems that have tendencies to associate into microstructures such as micelles. However this approximation, which is attributed to Flory (15), has been supported in the polymer field by experimental data. Other conformational features such as bond lengths and bond angles are initially set to their equilibrium values. These values generally adjust very quickly during the course of an MD simulation.

The initial distribution of torsion angles was determined by the following method. In Figure 3 we depict the skeletal bonds of a segment of the NPE molecule. The labels (ϕ_1, ϕ_2, ϕ_3, ..., ϕ_8) identify eight unique torsion angles. These are unique in the sense that the collinear sequences of four skeletal atoms are all different in these eight labeled torsion angles. A conformational energy map was determined for each of these torsion angles by rotating the angle through 360 degrees in 10 degree intervals while simultaneously relaxing all other degrees of freedom to achieve a root mean square force of below 1.0 kcal/ (Mole Angstroms). In this calculation we included the full interaction potential. The electrostatic interaction terms were computed using charges derived from the Q-Eq method applied to the lowest energy conformation. No attempt was made to alter the charge values in a self-consistent way while the torsion angle was swept through 360 degrees. This simplification is justified by the relatively small size of the electrostatic energy as compared to the van der Waals interactions and the uncertainty of the partial charge values.

A representative conformational energy map is shown in Figure 4 for the torsion angle ϕ_4. From this figure we readily identify two, nearly equal in energy, rotational isomeric states (RIS) at 90 and 270 degrees. Next, we determined the width of each RIS at the point 0.6 kcal/mole above the minimum. This number was used as the torsion angle tolerance, $\Delta\phi_4$, for constructing the amorphous structures. In Table II we list the values of the RIS minima and the respective tolerances for all eight torsion angles.

Amorphous structures were constructed with POLYGRAF's built-in Monte-Carlo algorithm for creating models of amorphous polymers. The procedure is essentially the same for single molecule or multiple molecule systems. The center of each molecule is placed in a random position within the unit cell and the structures are grown from the middle outwards. As the conformations are grown, several constraints are imposed. Hard overlaps are avoided by ascribing a hard core radius to each atom equal to 0.3 times the van der Waals radius. The periodic boundary condition is imposed in order to create amorphous systems at the required density. In these calculations, we have used the experimentally determined densities for our

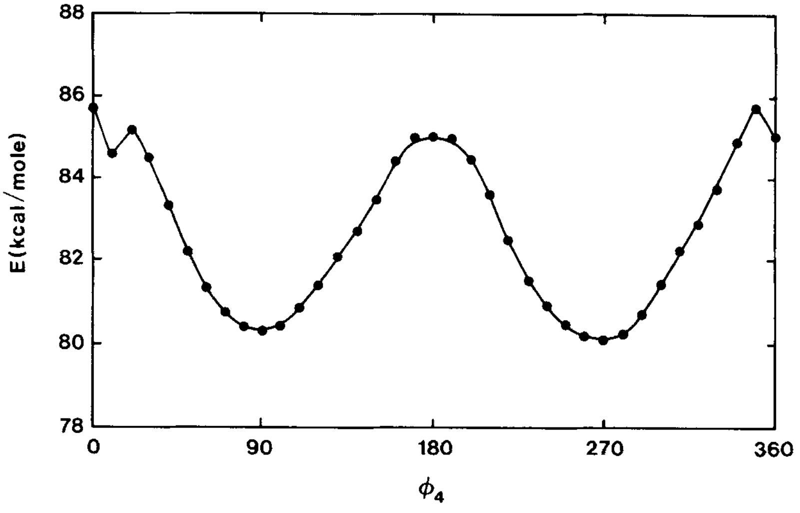

Figure 4 Conformational energy for the torsion angle labeled ϕ_4 in Figure 3. Two RIS state minima are identified at 90 and 270 degrees for ϕ_4.

Table II Rotational isomeric states for angles identified in Figure 3. The numbers given after the ± represent the full width of the RIS minimum at 0.6 kcal above the energy minimum.

Skeletal bond	*State 1*	*State 2*	*State 3*
ϕ_1	79.4 ± 19.1	183 ± 20.6	283.8 ± 19.2
ϕ_2	79.4 ± 22.6	179.4 ± 17.6	N/A
ϕ_3	91.2 ± 36.8	270.6 ± 38.2	N/A
ϕ_4	88.2 ± 22.1	270.6 ± 22.1	N/A
ϕ_5	179.4 ± 11.8	288.2 ± 20.6	N/A
ϕ_6	170.6 ± 25	285.3 ± 22.1	N/A
ϕ_7	79.4 ± 22.1	179.4 ± 13.3	279.4 ± 17.7
ϕ_8	88.2 ± 22.1	185.4 ± 21.4	N/A

model density (8). The final, and perhaps most important constraint imposed is the RIS state distributions. The molecular structures were grown with the torsion angle distributions determined from Boltzmann weighting of the energies of the RIS minima. Once the required RIS state distributions were known, the RIS states were populated allowing for the angle tolerances specified in Table II.

Molecular Dynamics Simulations

Once an ensemble of structures was prepared using the method described above, a conjugate-gradient energy minimization was performed in order to remove any strong van der Waals overlaps. This energy minimization step often uncovered conformation anomalies which resulted in the rejection of the conformation. In particular, since we used reduced van der Waals radii in the build process, we often encountered conformations where a phenol ring was threaded by either an alkyl or ethylene oxide portion of an image chain.

Following the energy minimization step, a series of constant energy/constant volume (NVE) MD simulations were performed on each structure. These MD simulations serve two purposes: to anneal the initial state configuration and to sample representative states. The procedure we used was somewhat different for the single chain models versus the multichain models. For the single chain models, the annealing simulations involved performing 10 picoseconds (ps) of NVE MD with a simulation temperature of 400 K. The 10 ps time frame is insufficient for the NPE-x molecules to undergo drastic conformational rearrangements, but is sufficient to undergo small numbers of torsional rotations. The annealing step was followed by a second energy minimization step which in all cases resulted in a significantly lower energy conformation when compared to the first minimization step. Following this second energy minimization step, a second NVE MD simulation at 300 K for a duration of 5 ps was performed. For the multichain models, a total of 100 ps of constant temperature (NVT) MD was performed at 300 K. The first 60 ps of the simulation was regarded as an equilibration or annealing time and the last 40 ps was used in the analysis described below. Finally, a single NPE-4 chain, in vacuum, was simulated for 1000 ps at 300 K in order to provide average values of the energy variables in the absence of intermolecular interactions.

3 RESULTS AND DISCUSSION

In Table III we summarize energy values for the NPE-4 system computed from MD simulations at 300 K. The second column tabulates the values derived from a single chain of NPE-4 in the vacuum. These numbers were computed by averaging the values in a 1000 ps MD simulation. The third column displays the values derived from eight NPE-4 chains in a periodic cell packed to a density of 1.022 gms/cc. These values were derived from averaging the values in the last 40 ps of a 100 ps MD simulation at 300 K. Column three values are divided by eight for easy comparison to column two.

As expected, the only significant differences occur in the van der Waals, electrostatic and hydrogen bonding energies. These differences represent the nonbonded energy associated with packing the molecules into the periodic cell and can, therefore be used to compute the cohesive energy and the three dimensional solubility parameters. The procedure for performing this calculation is given in reference (8).

The three-dimensional solubility parameters computed from the eight chain structure are listed in column two of Table IV. In column three we list the values computed from the group contribution method using the tables in van Krevelen's book (13,14). Ideally, our results should be compared to experimental values, which are unfortunately not readily available for many materials such as NPE-x. Group contribution methods, which are based on experimental data, were therefore used for comparison purposes. The agreement between the many chain calculation and the group contribution method is very good. The only discrepancy is in the values predicted for the polar parameter. The group contribution method is founded on the principle of pairwise additive short ranged interactions and is therefore not expected to be accurate for electrostatic interactions. These interactions are long

Table III A comparison of the average energies computed at 300 K for NPE-4 in the vacuum and the condensed state. The condensed state is modeled here using eight molecule structures in a periodic box as in Figure 2.

Energy variable	*Single Chain in Vacuum (kcal/mole)*	*Multiple Chains in the Bulk (kcal/mole)*
E_{total}	215.3 ± 8.3	183.6 ± 3.0
$E_{kinetic}$	58.2 ± 5.8	60.2 ± 2.1
E_{vdw}	40.2 ± 3.3	13.3 ± 1.4
E_{elec}	45.9 ± 1.5	41.3 ± 0.6
E_{hb}	0.0 ± 0.0	−6.4 ± 0.5
E_{bond}	25.9 ± 4.3	25.6 ± 1.5
E_{angle}	35.2 ± 4.4	37.7 ± 1.7
$E_{torsion}$	8.9 ± 1.7	11.1 ± 0.6
$E_{inversion}$	0.9 ± 0.6	0.9 ± 0.2

Table IV A comparison of three dimensional solubility parameters computed using single chain models, multiple chain models and group contribution tables.

Solubility Parameters	*Single Chain* $(cal/cc)^{1/2}$	*Multiple Chains* $(cal/cc)^{1/2}$	*Group Contribution* $(cal/cc)^{1/2}$
δ	10.4 ± 0.3	9.9 ± 0.5	9.6
δ_d	8.4 ± 0.2	8.3 ± 0.6	8.4
δ_p	4.6 ± 0.5	3.4 ± 0.6	1.2
δ_h	4.2 ± 0.2	4.1 ± 0.2	4.4

ranged and are also sensitive to local structure. In our calculations the predicted value of the polar solubility parameter is sensitive to the values of the electrostatic charges used in the potential energy function. This point was discussed in reference (8).

In column two of Table IV we list the computed values of the solubility parameters derived from using only a single chain in a periodic box of dimension 8.64 × 8.64 × 8.64 Angstroms. The dimensions of this box are chosen to give the same density as the eight chain system, which is the experimental density. The solubility parameters were computed in this case by computing the energy function with and without the periodic boundary condition. The periodic boundary condition serves to introduce intermolecular interactions between the parent chain and images of the parent chain. The entries in column two were computed from an ensemble average of 10 systems and a time average over 5 ps. The ± values indicate the ensemble fluctuations in the numbers and not a computational error estimate.

The values predicted using single chain systems are the same as those derived from using eight chains within the statistical fluctuations in the numbers. We believe that the agreement here stems from the great flexibility of the alkyl and ethylene-oxide portions of the NPE-4 molecule. Again the greatest discrepancy is with the polar solubility parameters which has contributions from very long-ranged interactions and would therefore be sensitive to the system size and periodic boundary condition. The calculation of the electrostatic interactions can also depend on the value of the interaction cut-off imposed. For the calculations

Table V Computed three dimensional solubility parameters of the NPE system as a function of temperature and ethylene oxide content. The NPE-x system has x units of ethylene oxide.

	NPE-4 *(cal/cc)*$^{1/2}$	*NPE-9* *(cal/cc)*$^{1/2}$	*NPE-15* *(cal/cc)*$^{1/2}$
0 K			
δ	11.0 ± 0.2	10.9 ± 0.3	10.7 ± 0.4
δ_d	8.9 ± 0.1	9.3 ± 0.4	8.9 ± 0.4
δ_p	4.6 ± 0.5	4.6 ± 0.4	5.1 ± 0.3
δ_h	4.4 ± 0.1	3.5 ± 0.4	3.1 ± 0.1
300 K			
δ	10.4 ± 0.3	10.4 ± 0.4	10.2 ± 0.5
δ_d	8.4 ± 0.2	8.8 ± 0.4	8.4 ± 0.6
δ_p	4.6 ± 0.5	4.5 ± 0.4	5.1 ± 0.4
δ_h	4.2 ± 0.2	3.2 ± 0.4	3.0 ± 0.2
400 K			
δ	10.0 ± 0.3	10.0 ± 0.6	9.9 ± 0.5
δ_d	8.1 ± 0.3	8.5 ± 0.6	8.0 ± 0.5
δ_p	4.4 ± 0.5	4.4 ± 0.5	4.9 ± 0.3
δ_h	3.8 ± 0.3	3.0 ± 0.6	2.8 ± 0.2

reported here we have used a cut-off of 100 Angstroms after establishing that the results were not sensitive to the cut-off beyond about 50 Angstroms. We observed differences of up to 100% in the value of the polar dispersion parameter if a shorter cut-off distance (10 Angstrom) is used. Since the units cells used in these calculations are also of the order of 10 Angstroms in size, the intermolecular interactions due to images of the unit cell will be very important.

In Table V we summarize the series of calculations on the NPE-x family of surfactants for $x = 4,9,15$ at temperatures of 0 K, 300 K and 400 K. The 0 K results reported here are energy values derived from repeated annealing and minimization steps as described earlier. Note that we did not correct the density of these systems to account for thermal expansion. All calculations were performed using the experimental densities determined at 300 K.

Several trends can be observed in Table V. For each temperature value there is no significant difference in the overall solubility parameter in going from $\chi = 4$ to 9 to 15. The dispersion solubility parameter doesn't show any trend with increasing ethylene oxide content. This is not too surprising since the addition of more ethylene oxide content (-CH_2-CH_2-O-) adds both more electrostatic interactions and dispersive interactions. The overall dispersive energy density is not greatly affected.

While there is an increase in the polar solubility parameter with increasing ethylene oxide content, there is also a decrease in the hydrogen bonding parameters which effectively cancels out the increase in the overall solubility parameter. The hydrogen bonding occurs only through the terminal OH group whose density decreases with increasing chain length.

For a given surfactant system in Table V, there is a small decrease in the solubility parameter with increasing temperature. Most of this temperature dependence arises from the decrease in van der Waals interactions. The weakening of the van der Waals interactions relative to the electrostatic interactions with increasing temperature is consistent with the observed phase behavior of these surfactants. As temperature is increased, an oil-in-water emulsion made with NPE-x undergoes a phase inversion to form a water-in-oil emulsion (1). We attribute this to a weakening of the interfacial dispersive forces relative to electrostatic forces.

Like the dispersion interactions, the hydrogen bonding displays a decrease in interaction strength with increasing temperature. This effect is a consequence of the potential energy function. In the present model, the hydrogen bonding interactions (Lennard-Jones 12-10) and van der Waals interactions (Lennard-Jones 6-12) are derived from similar functional forms.

4 SUMMARY

To summarize, we have used molecular mechanics models of the amorphous liquid state of a family of NPE-x surfactants to examine, in detail, the nature and strength of dispersive and electrostatic interactions. Three dimensional solubility parameters were computed from these models with good agreement with those derived from group contribution methods for the dispersive and hydrogen bonding parameters. The polar solubility parameters are much higher in our calculations than the group contribution method predicts.

Two different models of the amorphous liquid state were examined here. One set of models represented the amorphous liquid with an ensemble of single molecule conformations and a periodic boundary condition, as used by Theodorou and Suter (7). The results derived from these models were compared to those derived from models constructed using eight distinct molecular structures packed into a unit cell. The agreement between these two descriptions was excellent with significant differences appearing only for the polar solubility parameter. This parameter arises from very long ranged interactions and is consequently the most sensitive to system size effects.

For the NPE family, the dispersion solubility parameter we computed was insensitive to the amount of ethylene oxide content. Increasing ethylene oxide content does increase the polar solubility parameter, but also leads to a decrease in the hydrogen bonding solubility parameter. Most of the temperature dependence of the overall solubility parameter, or cohesive energy density, is due to the temperature dependence of the dispersive interactions.

The use of molecular force fields to compute three dimensional solubility parameters offers many advantages over the group contribution method and in many ways represents a generalization of the method. The group contribution method is founded on the notion of additive interactions and statistical contributions to property values. In the approach we have used here, although our intermolecular interactions are pairwise additive, they are not limited to short ranged interactions and they do depend on local structure. One can therefore address the role of stereoregularity, crystallinity, molecular association and polymorphism within this framework. Through the use of molecular dynamics, we are able to address the role of physical variables such as temperature and pressure on solubility properties as well.

There are at present some limitations to using this method for deriving thermodynamic parameters such as solubility parameters. Force field parameters are one of the current limitations. These parameters are, in general, optimized to predict a large number of experimental crystal structures and therefore only perform well in an average sense. As methods are developed to generate accurate force field parameters, the accuracy of the calculations reported here will improve as well. Another limitation of the molecular mechanics/dynamics approach is the presence of finite sized effects. In particular, the statistical mechanical fluctuations and very long ranged electrostatic interactions introduce uncertainties which can only be improved upon by studying larger systems.

In future work we will examine the enthalpies of mixing NPE surfactants with water and alkanes using molecular mechanics models. We will also consider the extension of the present approach to predict other thermodynamic parameters that are commonly used such as Flory-Huggins interaction parameters.

Acknowledgments

The authors would like to thank Dr J.P. Bareman and Dr. P.R. Sundararajan for helpful discussions. P. Choi and A. Rudin thank the Natural Sciences and Engineering Research Council of Canada and the Ontario Centre for Materials Research for financial support of this work and the Xerox Research Centre for their hospitality.

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