Molecular modeling of polymer composite–analyte interactions in electronic nose sensors

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Abstract

We report a molecular modeling study to investigate the polymer–carbon black (CB) composite–analyte interactions in resistive sensors. These sensors comprise the JPL electronic nose (ENose) sensing array developed for monitoring breathing air in human habitats. The polymer in the composite is modeled based on its stereoisomerism and sequence isomerism, while the CB is modeled as uncharged naphthalene rings with no hydrogens. The Dreiding 2.21 force field is used for the polymer, solvent molecules and graphite parameters are assigned to the carbon black atoms. A combination of molecular mechanics (MM) and molecular dynamics (NPT-MD and NVT-MD) techniques are used to obtain the equilibrium composite structure by inserting naphthalene rings in the polymer matrix. Polymers considered for this work include poly(4-vinylphenol), polyethylene oxide, and ethyl cellulose. Analytes studied are representative of both inorganic and organic compounds. The results are analyzed for the composite microstructure by calculating the radial distribution profiles as well as for the sensor response by predicting the interaction energies of the analytes with the composites.
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Keywords: Electronic nose; Polymer composite; Molecular modeling; Interactions

1. Introduction

The ability to monitor the constituents of air in a closed environment is important to NASA for controlling the breathing air quality in human habitats in which air is recycled. At present, air quality on space shuttle flights is determined by collecting samples and analyzing them on the ground using laboratory analytical instruments such as a gas chromatography–mass spectrometer (GC–MS). The availability of a miniature, portable instrument capable of identifying contaminants in the breathing environment at parts-per-million levels would greatly enhance the capability for monitoring the quality of recycled air as well as providing notification of the presence of potentially dangerous substances from spills and leaks. To fill this need, JPL is developing an electronic nose (ENose) for air quality monitoring [1–3].

An electronic nose is an array of chemical sensors which respond when exposed to vapors. Each sensor is non-specific to any one vapor. Upon exposure to a vapor, the sensors respond, creating a pattern across the array. The pattern of distributed response may be deconvoluted, and the contaminants identified and quantified using a software analysis program such as pattern recognition and/or neural network or principal component analysis. Electronic noses have been discussed by several authors and may be applied to quality control and environmental monitoring in fields such as food processing, medical and industrial environmental monitoring [2,3–11].

The electronic nose developed at JPL uses an array of polymer–carbon black composite sensing films [1–3]. The addition of carbon black to an insulating polymer matrix makes the film conducting. The conductivity is the result of the formation of carbon black conductivity networks in the polymer matrix. Upon exposure to organic vapors, the polymer matrix swells, resulting in the breaking of some of the carbon black conductive networks and hence causing a change in the sensor response [1,11].

The selection of sensors for an array should be based on the group of analytes one wishes to identify. Acquiring experimental data for one set of analytes and optimizing the array for selectivity, sensitivity and stability is time and labor intensive. If new analytes are selected, it would be convenient to be able to know a priori the predicted responses of potential sensors to these analytes; the array can then be optimized with less extensive experimental testing. An approach to selection based on molecular modeling will help not only in providing

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a fundamental understanding of the molecular level processes related to polymer composite–solvent interactions but also in setting protocols for optimizing the array matrix. Thus, theoretical and computational approaches coupled with experimental efforts will be a key in selecting and developing new improved materials in a more rational way [12].

The underlying objective of this work is to develop molecular models which accurately describe polymer–carbon black (CB) composite films used in the ENose sensors and to gain a detailed understanding of their interactions with target analyte molecules. Polymers considered for this work include poly(4-vinylphenol) (PVPh), polyethylene oxide (PEO), and ethyl cellulose (EC). The analytes studied are representative of both inorganic (ammonia and hydrazine) and organic (methanol and toluene) compounds and are target compounds for monitoring on the International Space Station. A combination of molecular simulation tools (molecular mechanics and dynamics) is used to obtain the composite model and also evaluate its interaction with analytes.

Section 2 of this paper describes the models for the polymer, carbon black and also outlines an approach used to develop the final composite model. The simulation details are discussed in Section 3. The microstructure details of the composite films and their interactions with the analytes are discussed in Section 4.

2. Molecular models

Molecular simulations were performed on a Silicon Graphics O2 workstation, using the commercial software Cerius[2] [13]. Simulation approaches include molecular mechanics (MM) and molecular dynamics with number of atoms, volume and temperature held constant (NVT-MD) and molecular dynamics with number of atoms, pressure and temperature held constant (NPT-MD).

2.1. Polymer

The polymer model is based on its stereoisomerism (tacticity) and sequence isomerism (connectivity). The polymer tacticity results in three possible arrangements of the side groups (or pendant groups) around the polymer backbone. The side groups could be on one side (isotactic), on alternate sides (syndiotactic) or randomly arranged (atactic) around the polymer backbone. The connectivity of the monomer units could be head-to-tail, tail-to-tail or head-to-head.

2.2. Carbon black (CB)

The CB structure typically consists of spheroidal particles fused to each other. Within each of these particles, carbon atoms are arranged in imperfect graphite layers [14]. The CB in the present work is modeled as naphthalene rings with no hydrogen, to mimic small graphite sheets, as it is difficult to insert large graphite sheets in a high-density polymer matrix.

2.3. Polymer–carbon black composite

Sensing films for the JPL ENose are made by dissolving the polymer in a solvent or solvent mixture, dispersing the carbon black in the polymer solution, pipetting the composite solution onto the sensor substrate, and allowing the solvent(s) to evaporate [1–3]. The model for the polymer–CB composite film is being developed by adopting a strategy that involves performing simulations first under "no solvent" and then under "solvent" conditions.

2.3.1. No solvent conditions

The composite model is initially developed under no solvent conditions (or vacuum). To begin with, the density of the polymer–CB composite film (ρ) is approximated as a linear combination of the sum of bulk density of individual components times their weight fractions, i.e. $\rho = \rho_p x_p + \rho_{cb} x_b$ (where ρ_p is the polymer density, ρ_{cb} the carbon black density, x_p the weight fraction of the polymer and x_{cb} the weight fraction of the carbon black). The densities and other physical characteristics of the different polymers and CB used in the current study are listed in Table 1. The JPL ENose films are made with polymer weight fraction of 0.75–0.8 [1–3]. A value of $x_p = 0.75$ was considered for the current composite model development. An amorphous polymer unit cell was built with a density $\rho_p x_p$ containing two polymer chains each containing m monomer units. The naphthalene rings were then inserted in the polymer matrix until the composite film density ρ was reached. The entire system is then equilibrated by MM followed by NVT-MD simulations at 300 K.

2.3.2. Solvent conditions

The composite structure obtained under "no solvent conditions" is then subjected to solvent conditions. The composite structure obtained from the previous step is immersed in a large solvent box. This step is done to mimic the polymer–carbon black solution, which is used in solvent casting of the sensor films. The entire system (composite + solvent) is

Table 1
Physical properties of polymer composite components

	Density (g/cm³)		Glass transition (°C)
	Polymer	Composite[a]	
Poly(4-vinylphenol)	1.163[b] (1.2)	1.322	150
Polyethylene oxide	1.127[b]	1.295	−67
Ethyl cellulose	1.138[b] (1.14)	1.297	43
Carbon black (Cabot Black Pearl 2000)	1.8	–	–

[a] Starting density for the composite model development.
[b] Predicted by molecular modeling. The manufacturer's experimental value is shown in the bracket.

then equilibrated by MM followed by NVT-MD simulations at 300 K.

2.3.3. Film formation

On reaching equilibrium, the solvent molecules are removed. This step corresponds to deposition of the film and evaporation of the solvent from the sensor film, as done under experimental conditions. The box is then compressed to the target density ρ, followed by density and structural relaxation using NPT-MD and NVT-MD simulations at 300 K, respectively, to achieve the final density and equilibrium structure.

3. Simulation

The total energy of a system is a sum of its kinetic and potential energies. While the system kinetic energy depends on the temperature, the total system potential energy (U_{total}) can be written as a superposition of short range valence ($U_{valence}$) and long range non-bonded interactions ($U_{non-bond}$).

$$U_{total} = U_{valence} + U_{non-bond}, \tag{1}$$

where the valence (or internal) terms consist of bond stretching (U_{bond}), bond-angle bending (U_{bend}), dihedral angle torsion ($U_{torsion}$) and inversion ($U_{inversion}$) terms

$$U_{valence} = U_{bond} + U_{bend} + U_{torsion} + U_{inversion}, \tag{2}$$

For the polymer composite, the valence term contribution to the potential energy comes from the polymer chains and the carbon black molecules. The non-bond interaction term includes polymer–polymer, polymer–carbon black and carbon black–carbon black interactions. The non-bond (or external) interactions consist of van der Waals (U_{vdw}) and electrostatic (U_Q) terms

$$U_{non-bond} = U_{vdw} + U_Q, \tag{3}$$

The U_{vdw} term takes into account the intermolecular interactions and the interactions between atoms that are separated by three or more bonds within a chain.

3.1. Building the amorphous polymer box

The amorphous polymer box is built by first constructing a polymer chain based on its tacticity and connectivity. The atactic nature of poly(4-vinylphenol) is assumed (i.e. phenol groups arrange randomly with respect to the carbon backbone). No such assumption is necessary for the polymers PEO and EC, which have no tacticity centers. Head-to-tail connectivity of the monomers is assumed for all the polymers. The number of monomer units (m) is selected so as to keep the number of atoms in the composite model close to two thousand.

The charges of isolated polymer chains are based on the charge equilibration method (Q_{eq}) [15]. The polymer chains were initially minimized by molecular mechanics and then by molecular dynamics for 10 ps (time step = 0.001 ps) at 300 K. This was then followed by running annealing dynamics for 10 ps, in which the system temperature is varied in cycles from one temperature to another and back again. In our case, temperatures were varied in increments of 50 K for a cycle from 300 to 500 K and back. This annealing was done so as to relieve the stresses in the polymer chain. The Dreiding 2.21 force field [16] was used for the polymers.

An amorphous unit cell containing one polymer chain and of density $\rho_p x_p$ was then built using the AMORPHOUS builder module in the software. The unit cell containing one polymer is replicated in the x direction to form a superlattice containing two polymer chains. The amorphous polymer box was then minimized by both MM and NVT-MD at 300 K before the naphthalene rings were inserted.

3.2. Polymer–carbon black composite model development

Carbon black, modeled as naphthalene rings with no hydrogens, small graphite sheets, is inserted into the polymer matrix by performing a cavity search in the polymer matrix. The carbon atoms of the naphthalene rings have no charge and were assigned graphite parameters [17]. A cavity of radius 3.5–4 Å was used to determine possible locations for the naphthalene rings in the polymer matrix. The cavity could be searched either by using a grid search or by random cavity search [18]. A random cavity search was used for this work. The naphthalene rings are inserted in the amorphous polymer box until a starting model density $\rho = \rho_p x_p + \rho_{cb} x_{cb}$ (as discussed in Section 3.1) of the composite is reached. Density and structural relaxation for the polymer–CB composite was then achieved by performing molecular mechanics followed by NVT-MD simulation at 300 K. The attainment of equilibrium was judged by monitoring the total energy of the composite. Equilibrium was assumed if the change in system potential energy was less than 5 kcal/mol over 50 ps simulation run.

The next stage in the composite model development involves equilibrating the composite model in the solvent. A unit cell with the desired solvent composition was initially created and minimized by MM. A superlattice of the solvent box was then created so as to have ~5000 solvent atoms in the system. The solvent box is then equilibrated by both NPT-MD and NVT-MD to get the equilibrium structure.

The composite structure was then immersed in the solvent box. Solvent molecules that are closer than 1.4 Å to the polymer and naphthalene rings were excluded to avoid infinite force problems. The composite structure was then equilibrated by MM to remove close contacts followed by NVT-MD. Upon achieving equilibrium, based on monitoring the total energy of the system, the solvent molecules are excluded and the box is recompressed to the starting density, ρ. The structure is then optimized again, using both NPT-MD and NVT-MD. Equilibrium was assumed if the change in potential energy of the system was <2 kcal/mol over 100 ps simulation run.
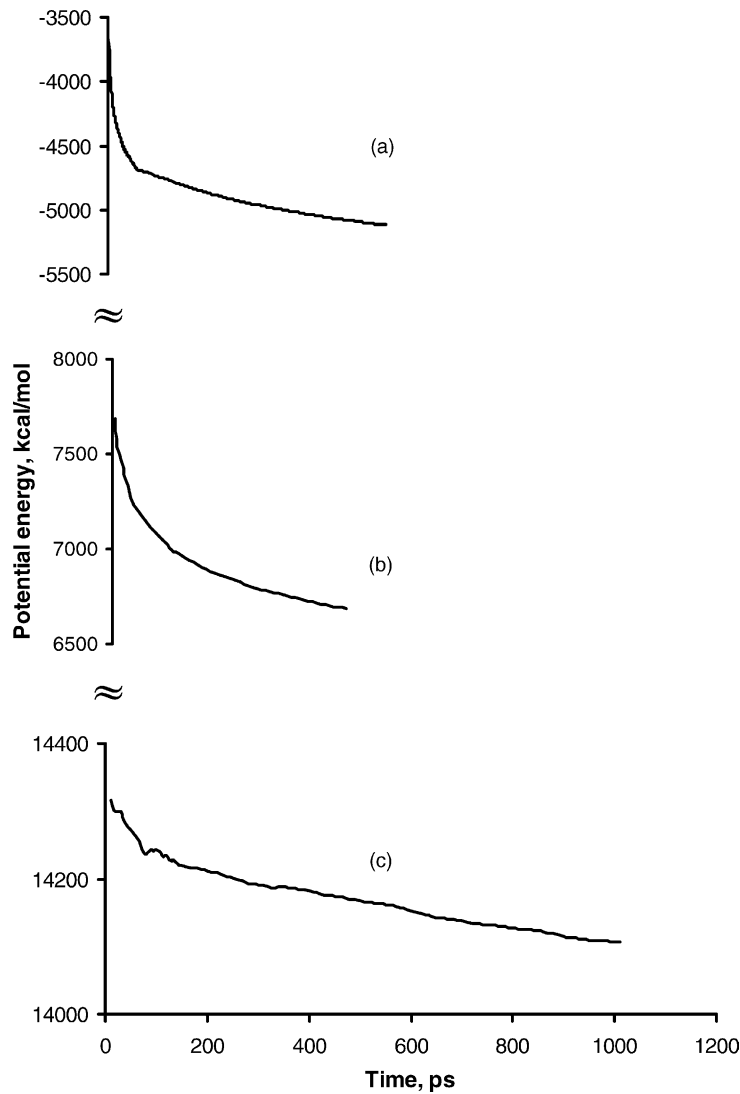
Fig. 1. NVT-MD equilibration of solvent–polymer carbon black composite systems for: (a) poly(4-vinylphenol), (b) polyethylene oxide, and (c) ethyl cellulose polymers.

4. Results and discussion

4.1. Development of the composite model

Immersing the composite in the solvent box mimics the composite solutions used for film casting. Fig. 1(a), (b) and (c) show the convergence of the potential energy of the composite structure in the solvent by performing NVT-MD simulations at 300 K using a time step of 0.001 ps.

Fig. 2 shows the density versus time plots of the composite after performing NPT-MD simulations at 300 K for the final structure. The final predicted densities are ordered, PVPh > EC > PEO. The convergence of the potential energy of these structures by NVT-MD simulations are shown in Fig. 3(a), (b) and (c). A comparison of the stability of these structures based on these energies is not possible because there are different solvent mixtures used for the film casting of each polymer. On average, the composite structures take a few nanoseconds of MD simulations to equilibrate.
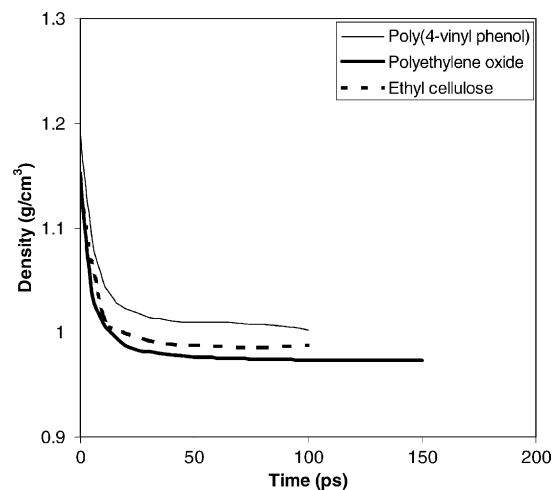

Fig. 2. Density vs. time plots of the composite obtained by NPT-MD equilibration after solvent removal from: (a) poly(4-vinylphenol), (b) polyethylene oxide, and (c) ethyl cellulose composite systems.
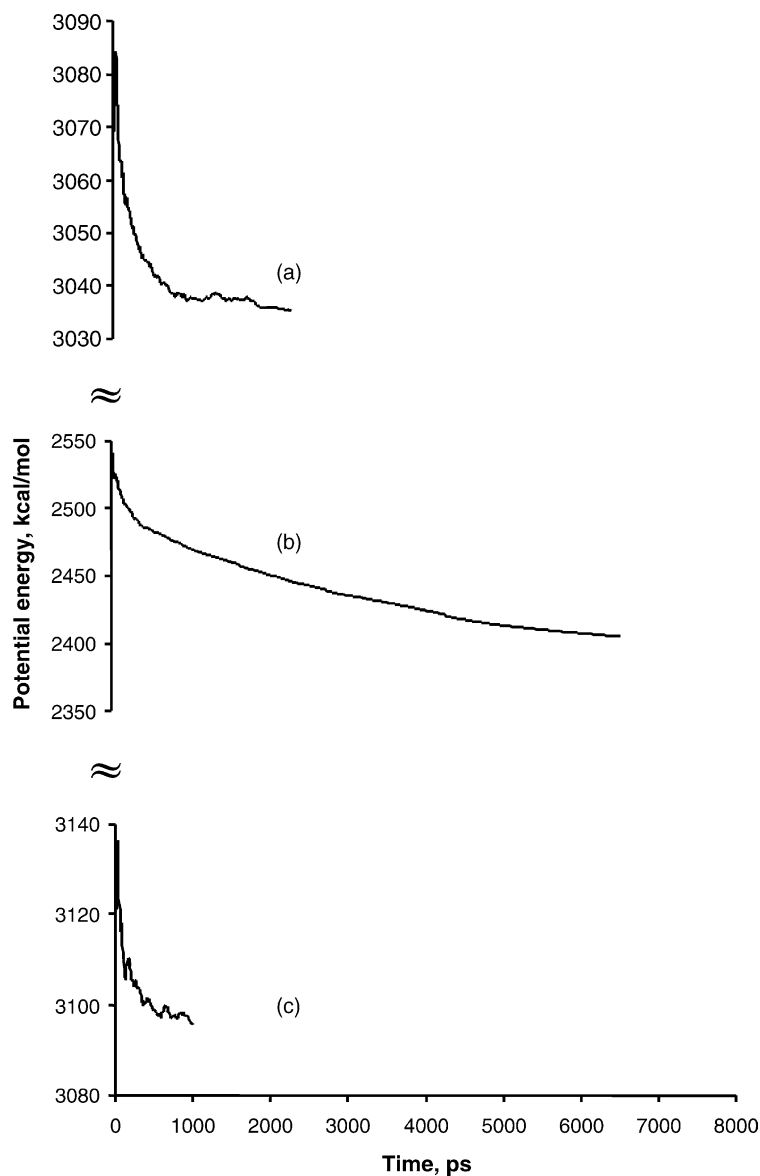
Fig. 3. NVT-MD equilibration of polymer carbon black composite after solvent removal from: (a) poly(4-vinylphenol), (b) polyethylene oxide, and (c) ethyl cellulose composite systems.

The PEO composite needs more time to equilibrate, compared to the other polymer composites. This could be due to the low glass transition temperature of PEO (as shown in Table 1), resulting in more flexibility of the polymer chains.

4.2. Analysis of polymer composite microstructure

Polymer composite microstructure can be evaluated by calculating the radial distribution profiles, $g(r)$, from the trajectories of the composite structure. The radial distribution function is the ratio of local density of the atoms to the system density. It gives the number of atoms found at a given distance in all the directions seen from an atom of interest [19]. We would like to know how the naphthalene rings arrange with respect to the polymer backbone in the

composite. This could provide an insight to the percolation behavior in polymer–CB composites where the addition of the CB imparts conductivity to the film by coating the polymer and also forming networks in the polymer matrix [20]. Fig. 4(a) shows the radial distribution function of the naphthalene rings with respect to the carbon atoms of the polymer backbone. The sp^3 hybridized carbon atoms on the polymer backbone were used for the radial distribution calculations of the PVPh and PEO polymers, while for EC, the carbon atoms that forms the cellulose backbone (ring carbon atoms) were considered for calculations. It can be seen that the naphthalene rings cluster more around the polymer backbone as compared to the other polymer composites. For the PVPh composite as shown in Fig. 4(b), the naphthalene rings tend to cluster around the phenol rings as compared to the polymer backbone.
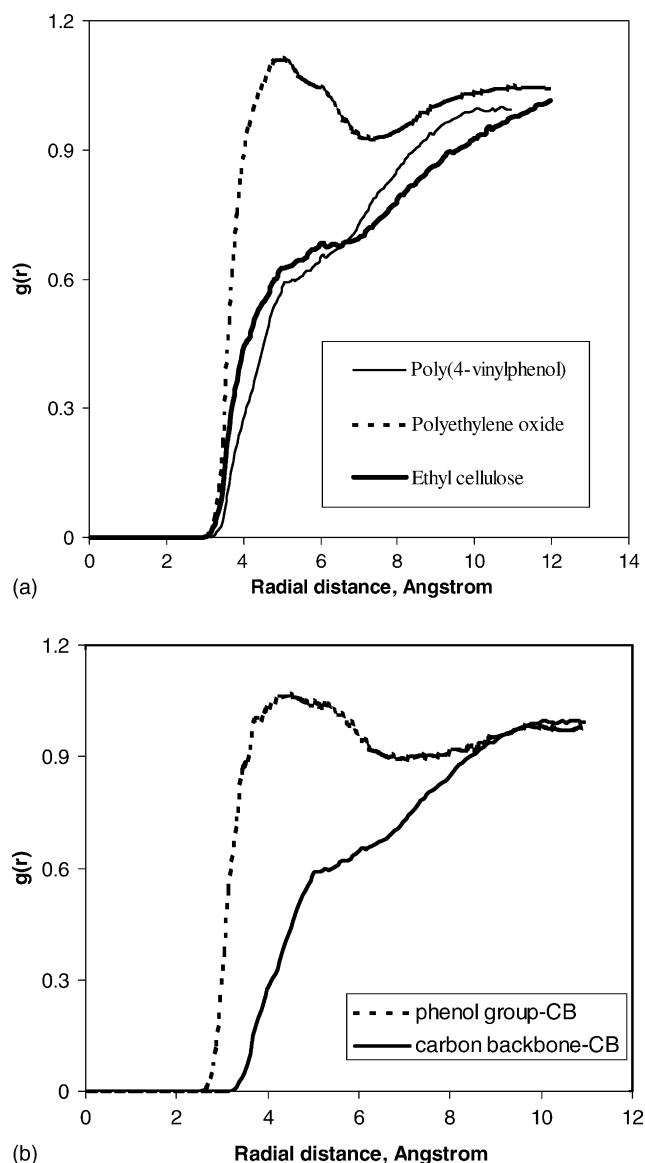
Fig. 4. Radial distribution profiles for naphthalene rings with the respect to the: (a) polymer carbon backbone for all composites, and (b) polymer carbon backbone and phenol oxygen atoms for the poly(4-vinylphenol) composite.

4.3. Interaction of analytes with polymer composite

The spacecraft maximum allowable concentration (SMAC) is the maximum concentration of an analyte permissible in the breathing air of a space-borne human habitat [21]. The 24 h SMAC for the analytes ammonia, methanol, toluene and hydrazine are 20, 10, 16, and 0.3 ppm, respectively. For most compounds, these concentrations are in single to tens of parts-per-million (ppm) range. It is difficult to perform sorption simulation studies at such low partial pressures of the analyte using the software (experiments being performed at atmospheric pressure) and could lead to no molecules being inserted into the system. Therefore, we considered one analyte molecule to calculate the interaction

energies of the analyte with the composites. The contributions to the total interaction energy of an analyte with the composite as shown in Eq. (4) is from its interactions with the polymer chains, CB molecules and other analytes. As there is only one analyte molecule, the analyte–analyte interactions will not contribute to total interaction energy.

$$U_{\text{composite-analyte}} = U_{\text{polymer-analyte}} + U_{\text{carbon black-analyte}} \quad (4)$$

The simulations were performed using the SORPTION module in the Cerius^2 software at a fixed loading of one analyte molecule, at 300 K. The program generates random points in the composite model and tries to insert the analyte molecules. Insertion attempts that involve the overlapping of the analyte molecule with the composite structure are discarded. For each composite–analyte interaction, 2–3 million simulations (analyte insertions) were run and the average energy of composite–analyte interactions was calculated at the end of the simulation. The interaction energies of the polymer composites with ammonia, methanol, toluene and hydrazine are shown in Fig. 5, respectively.

It can be seen in Fig. 5 that for the inorganic molecules ammonia and hydrazine, PEO composites show stronger interaction, as compared to the PVPh and EC composites. The organic molecules considered for the present study are methanol and toluene. The order of polymer composite–analyte interaction energy for methanol molecule is PVPh > PEO > EC. This may be caused by the strong hydrogen bonds that methanol can form with the first two polymers, PVPh and PEO, compared with bonds with EC. Toluene molecule shows a stronger interaction with the PEO composite compared with interaction with PVPh and EC composites.

Work is in progress for validating the above composite model with experimental findings.
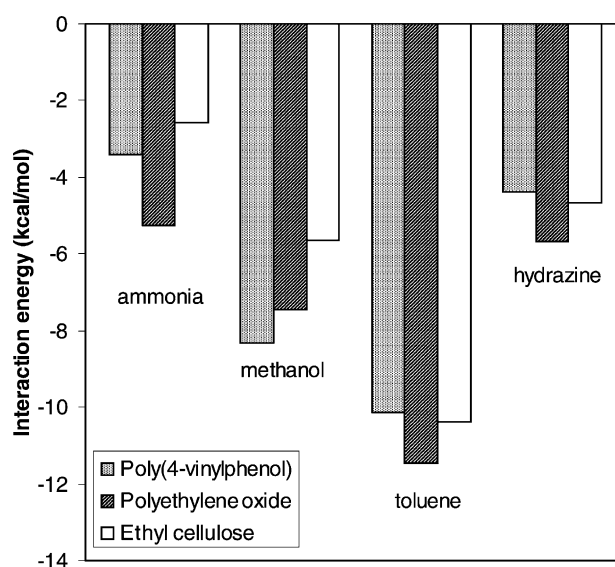

Fig. 5. Polymer composite–analyte interaction energies for ammonia, methanol, toluene and hydrazine molecules.

5. Conclusions

A molecular model for polymer–carbon composite sensing films was developed by an approach that mimics the experimental composite film casting and formation. The composite model consisted of carbon black modeled as naphthalene rings with no hydrogens inserted into an amorphous polymer matrix. Microstructure analysis using the radial distribution profiles showed the different arrangements of carbon black molecules with respect to the polymer backbone. Sorption studies at fixed analyte loading also predicted different composite–analyte interactions. Sensor response is a function of interaction energy, volume expansion as analyte enters the matrix, and the partition coefficient of the analyte in the polymer–carbon composite. This study is focused on the interaction energy alone; studies of volume expansion and partition coefficient are underway. Composite–analyte interaction energies predict that the PEO–carbon black composite is the sensor material with the strongest interaction energy with ammonia, toluene and hydrazine. PVPh has the strongest interaction energy with methanol.

Acknowledgements

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Biographies

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Margie Homer is the Co-Investigator of the Electronic Nose project at JPL. She obtained a BA in chemistry from Swarthmore College, Pennsylvania in 1985 and then a PhD in physical chemistry from the University of California at Los Angeles in 1993. Her research interest includes chemical sensors.

Allison Manfreda is a member of the JPL Electronic Nose team. She works on the experimental aspects of the ENose, including composite film casting and development, and training the sensors for different analytes. She received her BS degree in chemistry from California State Polytechnic University, Pomona in 2002. Her research interests include investigating

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Hanying Zhou is a member of the JPL ENose team. She develops data analysis programs to deconvolute the patterns of ENose distributed response. She received her MS in optical engineering from Zhejiang University, China in 1988 and a PhD in electrical engineering from the Pennsylvania State University in 1995. Between 1988 and 1990, she was a research scientist at Shanghai Institute of Fine Optics and Mechanics, Academia Sinica. Since 1998, she has been with the Jet Propulsion Laboratory where her main research interests include optical pattern recognition, holographic memory and sensor fusion.

Kenneth Manatt is a member of the JPL ENose team. He designs and programs the analog and digital electronics used in the JPL ENose sensor device. He received his BS in Geology from the University of California Santa Cruz in 1987. He has worked for numerous JPL programs since 1989 as an analog and digital electronics designer and programmer.