Developing Sensor Activity Relationships for the JPL Electronic Nose Sensors Using Molecular Modeling and QSAR techniques


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The JPL electronic nose (ENose) consists of polymer-carbon composite sensing films used to detect organic vapors and other environmental contaminants for Life Support and Habitation in space applications. The measured sensor responses are conductivity changes in polymer-carbon composite films upon exposure to target vapors (or analytes) at parts-per-million (ppm) concentrations. Training an array for a given set of analytes and a given set of environmental conditions (temperature, pressure, and humidity) is time consuming; in addition, developing training sets and calibration information may decrease the useful lifetime of the sensors. The ability to predict sensor responses accurately will be of great help in characterizing sensing materials.

Previous modeling studies to predict the response of polymer-film based sensors, primarily on pure polymer films, use Linear Solvation Energy Relationships (LSER) and solubility parameters to obtain a good correlation between the calculated and measured responses. Modeling efforts in the past for polymer-carbon composite sensing films based on solubility parameters, have taken into account only the effect of polymer-analyte interactions and assumed that neither carbon nor analyte in the film play a role in sorbing analyte molecules or in contributing to the response of the film. This model of sensor response may not represent a complete picture of response in polymer-carbon composite sensors.

We report a Quantitative Structure-Activity Relationships (QSAR) study using Genetic Function Approximations (GFA) with a unique molecular descriptor set, to describe the activities of the JPL ENose polymer-carbon sensors. In our work, the sensor activity for a given analyte is defined as the coefficient, $A_1$, which is correlated to the sensor response as $y = A_1x + A_2x^2$, where $x$ is the concentration of analyte. $A_2$ is generally three to five orders of magnitude smaller than $A_1$. The sensing activities of 4 polymer composite films (from an array of 16) are used for this QSAR study. The selected polymers fall in four categories (i) Hydrogen bond basic (ii) Dipolar and hydrogen bond basic Moderate dipolarity (iii) weak hydrogen bonding and weakly dipolar (iv) weak or no hydrogen-bonding. The unique QSAR descriptor set combines the default analyte properties (structural, spatial, topological, conformational, and thermodynamic) with descriptors for sensing film-analyte interactions, which describes the sensor response. The modeled analyte descriptors are calculated using QSPR techniques. The polymer-analyte interaction energies that describe sensor response are calculated using molecular modeling tools.

To test the approach, we have used the response of one of the sensor used in the JPL ENose, polyethylene oxide-carbon composite film, with 12% (wt/wt) carbon black. The analyte list is shown in Table 1. The training analytes set (#1-17) was used for the QSAR studies to develop the sensor activity equations. The statistically most significant QSAR equation among the set containing the polymer-analyte interaction term in combination with other descriptors was selected to represent the sensor. The selected QSAR equation was then used to predict the activity of test analytes not included in the QSAR training set and is shown in Figure 1. It can be seen that the model works satisfactorily for the benzene and dichloroethane but over predicts indole. It should be noted that through these QSAR equations we are only calculating a rough magnitude of the coefficients $A_1$. The calculated $A_1$ coefficients for analytes whose experimental data is not available, would provide a rough idea regarding the sensor response ($y = A_1x + A_2x^2$, where $x$ is the concentration). Since the coefficient $A_2$ is generally three orders of magnitude smaller than $A_1$, a low value of coefficient $A_1$ would imply weak sensor response to a given analyte. Hence a validated model (now under development) that correlates the coefficients with molecular descriptors will provide an a priori option of determining the activity of new analyte molecules without under going exhaustive experimental testing procedures.
Table 1: Analyte list and concentration range in parts-per-million (ppm) for the ENose operation (760 Torr and 23 °C).

1. Acetone (64-600)                        11. Ethylbenzene (20-180)
2. Ammonia (6-60)                           12. Freon113 (15-500)
3. Chlorobenzene (3-30)                     13. Hexane (15-150)
4. Dichloromethane (10-150)                 14. Methyl ethyl ketone (MEK) (15-150)
5. Ethanol (200-6000)                       15. Methane (1600-50000)
6. Isopropanol (30-400)                     16. Methanol (6-100)
7. Xylenes (33-300)                         17. Toluene (5-50)
8. Tetrahydrofuran (13-120)                 18. Benzene (10-100)
10. Acetonitrile (1-25)                     20. Dichloroethane (10-100)

Figure 1: A plot of calculated versus experimental sensor activity for the training set (17 organic vapors) and test analyte set using the combined descriptor set. The calculated values for both the training and test analyte set are obtained using equation, Calculated activity = 0.15207 E_{pa} + 0.117 HB_D^2 + 2.4 \times 10^{-4} MR^2. We observe that the analyte descriptors that also appear along with the polymer-analyte interaction term (E_{pa}) are hydrogen bond donor (HB_D) and molar refractivity (MR).