

# ADVANCED CHEMISTRY BASINS MODEL TECHNICAL REPORT

- Covering the period from June 10, 2000 – Dec 10, 2000
- Compiled by Peter Meulbroek
- Sections written by Mario Blanco, Lawrence Cathles, Paul Manhardt, Peter Meulbroek, and Yongchun Tang.
- Issued January, 2001

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## EXECUTIVE SUMMARY

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The advanced Chemistry Basin Model project has been operative for 18 months. During this period, most project tasks are on projected schedule (up to 150% of goals), with the exception of maturity indicators. On average the project is right on schedule (100%).

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## MILESTONE SCHEDULE/STATUS

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The only milestone listed in the project is to have a prototype model operational on a workstation. Progress towards that goal has been substantial (as detailed below) and on schedule. The prototype should be operational for the project annual meeting in June.

### TASK 1: MATURITY INDICATORS

<i>Primary Responsibility</i>	<i>Current Subtasks</i>	<i>Investigator</i>
Caltech	Develop algorithms	Tang

- *Summary:* The first task is to “Develop a database of additional and better maturity indicators for paleo-heat flow calibration”. Fundamental to this development is to perform a series of controlled kinetic experiments on maturity indicator evolution. The second year subtask is to “study  $R_0$  suppression, Compare thermal indicators, and Finish the  $R_0$  Database”.
- Tie maceral (H/C, H/O) composition to  $R_0$  kinetics (year 3)
- Generate Pyrolysis GC data (Gas/Oil Ratio, Paraffin Distribution) (year 3)
- Complete proposed number of samples for the  $R_0$  Database (year 4)

*Maturation Indices:* Kinetic parameters were determined for the  $C_{29}$   $5\alpha(H),14\alpha(H),17\alpha(H)$  sterane epimer ratio  $20S/(20S + 20R)$ , the  $17\alpha(H),21\beta(H)$  homohopane epimer ratio  $22S/(22S + 22R)$  and the  $C_{29}$  C-ring monoaromatic (MA)/ $C_{28}$  ABC-ring triaromatic steroid hydrocarbon (TA) parameter  $TA/(TA + MA)$ . Biological marker data used for these calculations were obtained from sedimentary basins with well-characterized burial and geothermal histories. The “EASY % $R_0$ ” kinetic model of Sweeney and Burnham (1990) was used for calibration purposes.

An investigative study of other maturity indicators commonly employed for the assessment of thermal histories of sedimentary rocks, including the methylphenanthrene index (MPI-1), smectite to illite conversion in shales and the thermal annealing of fission tracks in apatite, was initiated. Literature reviews have been started.

*Vitrinite reflectance kinetics database:* Vitrinite reflectance ( $R_0$ ) kinetics have been determined for six (5) different kerogens. Pyrolysis experiments were carried out in sealed gold tubes at two different heating rates.

*Vitrinite suppression:*  $R_o$  kinetics have been derived for liptinite-rich type II and type III kerogens. By combining  $R_o$ -temperature data for these two kerogen end members, we can now correct for vitrinite suppression in mixed type II-III kerogens.

### TASK 2: COMPOSITIONAL MATURATION

<i>Primary Responsibility</i>	<i>Subtask</i>	<i>Investigator</i>
Caltech	Establish a reaction network	Tang

*Summary:* The second task is to “Develop maturation models capable of predicting the chemical composition of hydrocarbons produced by a specific kerogen as a function of maturity, heating rate, etc.; assemble a compositional kinetic database of representative kerogens.” For the second year of the project, the sub-task is to “Expand and Modify the reaction network developed in Year 1”.

*Gas generation from Kerogen:* We have completed experiments on five different kerogen samples for gas generation using gold tube pyrolysis. Gas formation rates for C1, C2, C3, C4, CO<sub>2</sub> and H<sub>2</sub>S have been quantified. The data will be used to calibrate our kinetic model for primary gas generation.

*Hydrocarbon primary generation:* We have compared both simple and complicate hydrocarbon generation models. The 13 member of hydrocarbon formation from our previous work have shown consistent results in terms of kinetic fittings. Still to be determined is the transfer function from compositional information into basin oil property prediction.

### TASK 3: EQUATION OF STATE FLASH CALCULATION

<i>Primary Responsibility</i>	<i>Subtask</i>	<i>Investigator</i>
Caltech	EOS model	Meulbroek

*Summary:* The third task of the project is to “Develop a 4 phase equation of state-flash model that can define the physical properties (viscosity, density, etc.) of the products of kerogen maturation, and phase transitions that occur along secondary migration pathways.” For the second year of the project, the sub-task is to: “Determine Henries Law coefficients controlling maturation product interaction with the aqueous phase, and develop a prototype of full computational scheme.”

The two-phase equation-of state model previously developed in *Mathematica* has been ported to perl, a scripted, platform independent language that can communicate with the other pieces of the project. The porting is a major accomplishment necessary for the complete prototype. The model will be adapted to use COM, a Microsoft technology that eases communication between programs. A database has been implemented to store properties of oil components. Currently, the model relies on a database of 1500 possible oil compounds.

A pseudo-component-based viscosity model has been developed by the Tang group that requires very small sample sizes. This will be incorporated into the basin model during the next project year.

#### TASK 4: CONVENTIONAL BASIN MODELING

<i>Primary Responsibility</i>	<i>Subtask</i>	<i>Investigator</i>
Cornell	2-D model	Cathles
Cornell	add maturity indicators	Cathles

*Summary.* The fourth task of the project is to “Build a conventional basin model and incorporate new maturity indicators and data bases in a user-friendly way”. For the second year of the project, the sub-task is to “test code, and Incorporate additional kinetic data bases”. This has been slowed somewhat by the unforeseen difficulties in other sections of the project (see the June 10, 2000 report).

The conventional basin model is implemented except for erosion, where there is a bug in the NT code (a bug not present in the original Macintosh prototype). A great deal of work was expended (in the 3d half-year) to implement regridding schemes. Based on the results of tests performed with the new scheme, we have concluded the best approach for the DOE model will be grid refinement in the faults rather than re-gridding across the faults. This will simplify the models (from the user point of view) considerably. From a user point of view, regridding is just too complex, and there is no way to simplify the procedures. Our aim is to have a simple and easy to use advanced chemistry model that does not require an expert modeler to operate, so grid refinement seems the best option given the goals of the project.

Vitrinite reflectance maturity indicators are imbedded in the model. The framework for simple biomarker maturity indicators has been established and we are awaiting a trial  $R_0$  database. However, based on developments discussed below, I now feel that organic indicators based on changes in oil chemistry may be best incorporated as part of the hydrocarbon chemistry modeling (see below).

#### TASK 5: PRIMARY MIGRATION

<i>Primary Responsibility</i>	<i>Subtask</i>	<i>Investigator</i>
Cornell	2-D model	Cathles
Cornell	prototype algorithm	Cathles

*Summary.* The fifth task of the project is to “Develop an algorithm which combines the volume change and viscosities of the compositional maturation model to predict the chemistry of the hydrocarbons that will be expelled from the kerogen to the secondary migration pathways.” For the second year, the subtask is to “explore chemical feedback in primary flow”. This algorithm has been implemented combining both traditional concepts of primary migration—that primary migration is a response to changes in volume due to hydrocarbon maturation—as well as the new concepts relating to capillary effects.

A prototype primary migration algorithm is complete, as reported previously. In the past six months, Yuling Zheng has since developed a stand-alone Matlab prototype version of the model with a windows interface. He will use this to scientifically explore the functionalities of the primary migration algorithm, especially how long the expulsion of oil may be delayed from time of maturation. This work will verify and extend the algorithms already in the DOE model, and point the way to their proper integration with the secondary migration algorithms. For now we will assume that oil and gas migrate along secondary migration pathways as soon as they are produced in sufficient volumes to be mobile according to conventional relative permeability criteria.

#### TASK 6: SECONDARY MIGRATION

<i>Primary Responsibility</i>	<i>Subtask</i>	<i>Investigator</i>
Cornell	Develop prototype	Cathles

*Summary.* The sixth task of the project is to “Develop an algorithm that predicts the flow of hydrocarbons along secondary migration pathways, accounts for mixing of miscible hydrocarbon components along the pathway, and calculates the phase fractionation that will occur as the hydrocarbons move upward down the geothermal and fluid pressure gradients in the basin.” The first year sub-task is to “Develop prototype chemical advection algorithm linked to finite element models”. An algorithm has been developed that includes migration based on buoyancy with migration based on pressure gradients.

A prototype secondary migration algorithm should be by the end of the fiscal year on schedule. Algorithms have been completed that deconstruct the bulk "oil" and "wet gas" components that are predicted by our previously-completed maturation models into the 40 or more oil components needed for a flash calculation. A stoichiometrically balanced oil decomposition model has been completed and joined to this maturation/deconstruction model. The dynamic link library protocols that are required to communicate hydrocarbon P-T-X data to a C-language flash model are being developed. The flash model will return the molar volumes of the liquid and vapor (if any) phases. The migration algorithm will then redistribute the hydrocarbons until no element is over-filled, as described in the proposal.

#### TASK 7: INTEGRATION ON PC

<i>Primary Responsibility</i>	<i>Subtask</i>	<i>Investigator</i>
Geogroup	connect external code	Manhardt

*Summary.* The final task for the project is to “Integrate the above components into a functional model implemented on a PC or low cost workstation.” For the first year, the subtask is to “Develop mechanism for connecting external C or FORTRAN algorithms into PC system and train others in the code requirements.” This task has been satisfactorily completed. The code will be implemented on a PC running Microsoft Windows NT, and the different sub-programs will connect using ActiveX communication mechanisms.

Progress continues. Tests have been successful to date utilizing several cases from the US Gulf of Mexico. The tests should be complete by April 2001. A focus of the next period (Dec. 2000 – June, 2001) will be integration between the flow model and the chemistry model.

## The MS-Q Force Field for Clay Minerals: Application to Oil Production,

Sungu Hwang, Mario Blanco, Ersan Demiralp, Tahir Cagin, and William A. Goddard III,  
Submitted to The Journal of Physical Chemistry.

The equilibrium thermodynamics of chemical sorption of organic compounds on reservoir rock materials has been investigated. Sorption thermodynamics, energetics, are useful to model the migration of organic species over a period of time as a function of temperature and pressure. Knowledge is also needed of the structural changes in the clay material upon chemical sorption events and the interaction of the various clay layers with organic materials. Accordingly we have recently conducted molecular modeling work that pertains the thermodynamics of chemisorption of organic substances on clay minerals. We report a brief summary of this research below.

On a closely related area, specific progress has been made on the application of molecular simulations to study oil production chemicals including corrosion inhibitors,<sup>1</sup> scale inhibitors<sup>2</sup> and dissolvers.<sup>3</sup> So far, the focus has been on the mechanism by which these oil field chemicals act to inhibit corrosion and scale. Thus, we have considered the interaction between these chemicals with their target materials (Barite crystals for scale inhibitors and scale dissolvers, or mild steel surfaces for corrosion inhibitors.). However, it is also necessary to consider the interaction of these oil field additives with the reservoir rock surfaces. Of particular interest is the ability to tune the strength of the molecular sorption processes into the formation rock so as to increase the time period over which oil production additives are kept at the appropriate concentration in the oil (squeeze treatments for scale control and corrosion inhibition).

Among the minerals present in the walls of oil reservoirs, clay minerals are believed to be the most important because of their specific surface area and electric charge density. The sorption of oil field chemicals on clays and the slow release of the chemicals into the reservoir are important in determining the lifetime of the inhibitor. A better understanding of the interaction between clays and these chemicals is necessary to unravel the mechanism of squeeze treatments, to evaluate the treatment lifetime, and to make the optimum choice of a treatment strategy based on rock mineral composition.

Understanding the interaction between organic molecules and clay minerals is also important in other areas. An important one is an enhanced oil recovery process. Surface energies and the water and oil wettabilities of the exposed clay minerals are of great importance in heavy oil retention processes. Adsorption of polar compounds, such as asphaltenes, greatly affects the wetting properties of clays and thus the production capacity of the reservoir over time. Consequently, the simulation of the adsorption of squeeze treatment chemicals and hydrocarbons on clay minerals, which directly addresses the mechanisms of retention by the reservoir rock formation, should help evaluate crude oil recovery expectations and shall improve the ability to choose suitable oil recovery and field treatment strategies.

### Force Field Parameter for Clay

We begin with the MS-Q forcefield (FF) developed for describing bulk SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> systems by Demiralp et al.<sup>4-7</sup> This FF allows the atomic charges to readjust as a function of the instantaneous geometry using the charge equilibration (QEq) procedure<sup>8</sup> of Rappé and Goddard. In addition to electrostatic interactions, MS-Q uses a two-body Morse function to describe nonelectrostatic terms.

$$E_{ij}^{Morse}(R_{ij}) = D_0 \left\{ \exp \left[ -g \left( \frac{R_{ij}}{R_0} - 1 \right) \right] - 2 \exp \left[ -\frac{g}{2} \left( \frac{R_{ij}}{R_0} - 1 \right) \right] \right\} \quad (1)$$

The parameters for Si, O, and Al were taken from the previous work for the silicate and

aluminophosphate.<sup>4-7</sup> The FF parameters for hydrogen were optimized to reproduce the structural

parameters for kaolinite and pyrophyllite. The optimized parameters are listed in Table 1 and Table 2.

This type of forcefield has been successfully applied to predict structural changes upon external pressure loads on the polymorphism of silicates and aluminophosphates.<sup>4-7</sup>

**Table 1.** Diagonal Morse type van der Waals potential.

Atom types	$R_o$	$D_o$	$\gamma$	Note
H_C	3.3472	0.3796e-4	12.0000	Hydrogen
O_3C <sup>a</sup>	3.7835	0.5363	10.4112	Oxygen(hydrogen bonding donor)
O_AC <sup>a</sup>	3.7835	0.5363	10.4112	Oxygen(hydrogen bonding acceptor)
Al3C <sup>a</sup>	3.8915	0.3321	11.9071	Aluminum
Si3C <sup>a</sup>	3.4103	0.2956	11.7139	Silicon

<sup>a</sup>These force field parameters are taken from reference <sup>4-7</sup>.

**Table 2.** Off-diagonal Morse type van der Waals potential.

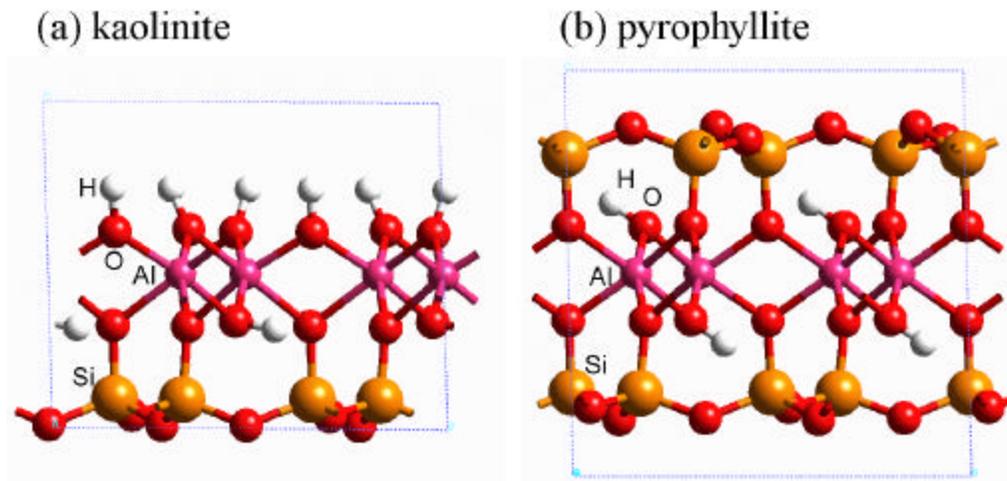
Atom types	$R_o$	$D_o$	$g$	Note
O_AC ... O_3C <sup>a</sup>	3.7835	0.5363	10.4112	
Al3C ... O_3C <sup>a</sup>	1.7775	26.03	9.7830	
Al3C ... O_AC <sup>a</sup>	1.7775	26.03	9.7830	
Si3C ... O_3C <sup>a</sup>	1.6248	46.00	8.3022	
Si3C ... O_AC <sup>a</sup>	1.6248	46.00	8.3022	
O_3C ... H_C	1.0770	19.55	8.4394	
O_AC ... H_C	2.1768	0.1753	16.0000	
Si3C ... Al3C <sup>a</sup>	4.0949	0.0000	8.7732	

<sup>a</sup>These force field parameters are taken from reference <sup>4-7</sup>.

Kaolinite has a 1:1 layered structure with one silicate tetrahedral sheet alternating with one octahedral sheet. Pyrophyllite is of a dioctahedral 2:1 type, which has 2 tetrahedral sheets and 1 octahedral sheet. The crystal structure parameters for kaolinite were taken from the neutron scattering experiments of Bish performed at 1.5 K.<sup>9</sup> Those of pyrophyllite were taken from the X-ray experiment of Lee and Guggenheim for one layer triclinic (1Tc) form.<sup>10</sup>

### 3.0 Results: Structure of clays

The simulation results for kaolinite and pyrophyllite are in excellent agreement with the neutron scattering<sup>9</sup> (kaolinite) and X-ray crystallographic<sup>10</sup> (pyrophyllite) experiments, as shown in Table 3 and Table 4. The MS-Q optimized structures are shown in Figure 1.



**Figure 1.** MM optimized structures of a) kaolinite and b) pyrophyllite.

**Table 3.** Comparison of the optimized structure of kaolinite with the experimental neutron scattering data.

	this work (MM)	exp. (1.5K) <sup>a</sup>
a	5.095	5.1535
b	8.840	8.9419
c	7.567	7.39036
Density	2.607	2.60835
O(donor)-H	1.02	0.977
O(acceptor)-H	2.22	2.2005
RMS deviation from exp.	0.118 (0.116*)	

\* FOR NON-HYDROGEN ATOMS

<sup>a</sup>reference <sup>9</sup>

**Table 4.** Comparison of the optimized structure of pyrophyllite with the X-ray data.

	this work (MM)	exp. (X-ray) <sup>a</sup>
a(Å)	5.119	5.160
b(Å)	8.905	8.966
c(Å)	9.214	9.347
density(g/cm <sup>3</sup> )	2.898	2.815
RMS deviation from exp. (Å)	0.07*	

\* For non-hydrogen atoms

<sup>a</sup>reference <sup>10</sup>

### Adsorption Enthalpies for Hydrocarbons on Clay

The sorption of hydrocarbons on clay surfaces is the key to the use of clays in the discovery, recovery, and processing of petroleum. Consequently, it is important to ensure that such interactions are modeled with high accuracy. To validate the FF, we performed molecular mechanics studies of the enthalpies of adsorption of 13 linear, branched, and cyclic aliphatic hydrocarbons on the surface of pyrophyllite clay, and compared the results with experiments<sup>11,12</sup> performed for smectite montmorillonite, a closely related dioctahedral smectite mineral. The heats of adsorption were taken from gas chromatographic retention volumes measured at 423 K. At this relatively high temperature, it is considered that nearly all the interlayer water has been removed and the clay layers are collapsed to just the size of the interlayer cation. Therefore it is reasonable to assume that the hydrocarbon uptake is minimal within the interlayer and that water and inner layer cations need not be included in the simulation.<sup>12</sup>

The results from molecular mechanics (MM) are listed in Table 6 and plotted in Figure 2. The results show a high correlation coefficient ( $R^2 = 0.97$ ) between experimental and calculated values, which suggests that our FF reproduces the experimental binding energies.

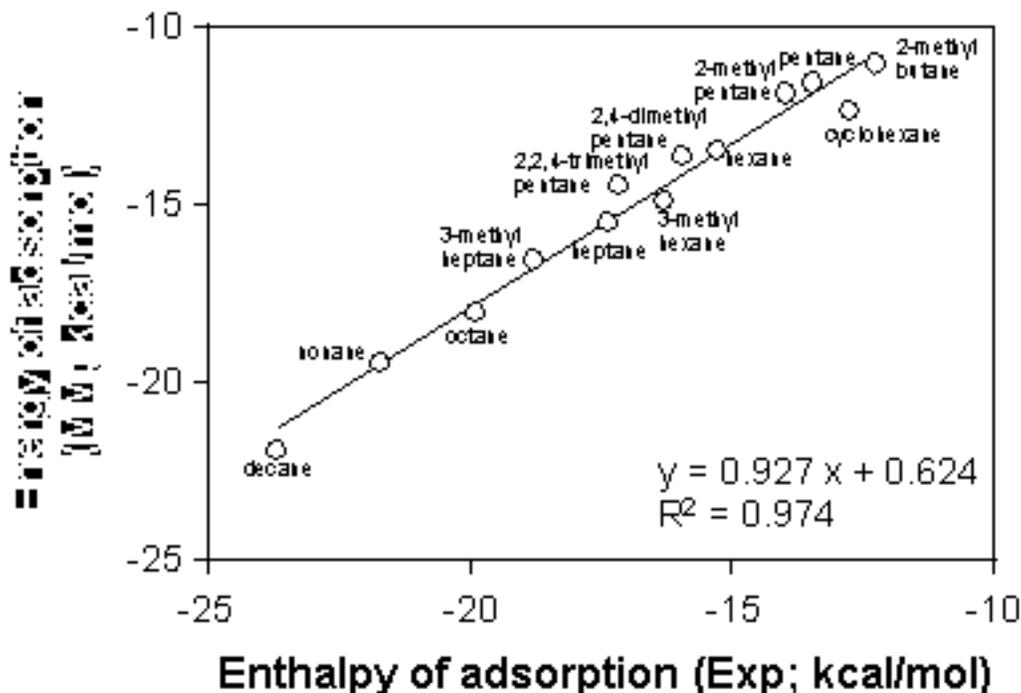
**Table 6.** Experimental and calculated enthalpies of adsorption. (kcal/mol)

	hydrocarbon	$\Delta E$ (MM) <sup>a</sup>	$\Delta H$ (exp, 423K) <sup>b</sup>	Error	$\Delta E$ (fit) <sup>c</sup>
1	2-methylbutane	-11.08	-12.3	1.2	-10.54
2	cyclohexane	-12.36	-12.8	0.4	-12.29
3	pentane	-11.58	-13.5	1.4	-11.53
4	2-methylpentane	-11.90	-14	2.1	-12.59
5	hexane	-13.47	-15.3	1.8	-13.58
6	2,4-dimethylpentane	-13.65	-16	2.3	-13.65
7	3-methylhexane	-14.89	-16.3	1.4	-14.64
8	2,2,4-trimethylpentane	-14.43	-17.2	2.8	-14.43
9	heptane	-15.54	-17.4	1.8	-15.63
10	3-methylheptane	-16.58	-18.8	2.2	-16.69
11	octane	-18.02	-19.9	1.9	-17.67
12	nonane	-19.42	-21.7	2.3	-19.72
13	decane	-21.88	-23.7	1.8	-21.77

<sup>a</sup>An isolated molecule on the surface of a  $4 \times 2 \times 1$  unit cell.

<sup>b</sup>Low coverage limit from reference <sup>11,12</sup>

<sup>c</sup>Based on Equation (3)



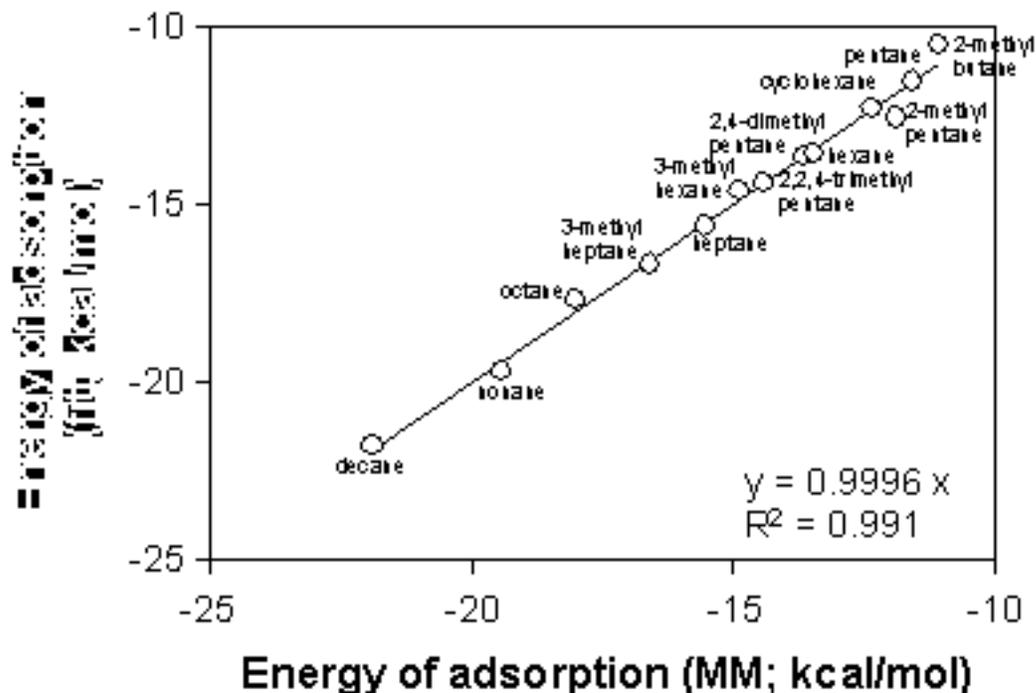
**Figure 2.** Plot of calculated heats of adsorption from energy minimization versus experimental values

We analyzed further the binding energy with a group additive approach to obtain a simple equation for adsorption energies of hydrocarbons on clay surfaces. (See Figure 3) The least square fitting to the energy of adsorption obtained from MM gives relationship as follows:

$$E_{\text{adsorption}} = -2.691 n(\text{CH}_3) - 2.049 n(\text{CH}_2) - 0.418 n(\text{CH}) + 1.498 n(\text{C}),$$

$$R^2 = 0.991, \quad (3)$$

where  $E_{\text{adsorption}}$  is the energy of adsorption per adsorbate molecule (in kcal/mol),  $n(\text{CH}_3)$  is the number of methyl carbon in the adsorbate,  $n(\text{CH}_2)$  the number of methylene carbon, and so on. .



**Figure 3.** Plot of calculated heats of adsorption from least-square fitting versus those from energy minimization

### Discussion

We have shown that with the appropriate choice of a force field it is possible to model not only the structural features of key minerals but also the sorption energetics of organic compounds, such as hydrocarbons, as well as the enthalpies of immersion of clays into polar and nonpolar solvents.

Based on the mineral rock composition of a specific reservoir one can envision the use of these thermodynamic data for calculations on extended retention times, or gradual release. Furthermore, one may use the insight gained from these simulations to help developed enhanced recovery. The molecular dynamics of oil and water phase flow over chemically modified clay surfaces can form the basis for a rational design of hydrodynamic surface modifiers in the same way that the modeling of organic additives on metal surfaces has helped the discovery of novel metal wear inhibitors.<sup>17,18</sup>

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