Adsorption Studies of Natural Gas Storage in Devonian Shales

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Summary

Significant amounts of natural gas exist as an adsorbed, or condensed, phase in Devonian shale formations and other unconventional gas resources. The amount of the adsorbed phase depends on the pressure and temperature. The Langmuir isotherm has been used to describe the pressure dependence. However, temperature dependence has not been explored. This is important to evaluate thermal stimulation as a recovery method and to extrapolate laboratory measurements to reservoir conditions. We investigate adsorption as a function of both pressure and temperature. We found that the effects of temperature are significant and that the Langmuir model does not describe adsorption adequately. We reconciled the data with bi-Langmuir models.

Introduction

Large amounts of natural gas accumulations exist in the Devonian shale formations of the Appalachian, Michigan, and Illinois basins. Several thousand trillion cubic feet of gas are estimated to be contained in this area.[1] The gas storage mechanisms in Devonian shale formations are quite different from those in conventional gas reservoirs. Natural gas is believed to be stored as an "adsorbed" phase on the shale matrix and organic materials, and as conventional "free" gas in the porous space. Experimental measurements have indicated that more than 50% of the total gas storage in the Devonian shales may exist as an adsorbed phase.[2-4]

Modeling the adsorbed phase can effect selection of stimulation techniques as well as production forecasts.[5,6] Adsorption generally cannot be determined accurately from history matching production data alone.[6] A well-test design has been developed for that purpose,[7] but it has yet to be demonstrated in the field. The laboratory testing of actual shale samples from reservoir cores is important for characterizing adsorption.

Previous laboratory studies have reported data from measurements at single temperatures, and the measured data have been represented by Langmuir isotherms.[2,3,8] While there is evidence that such representations can describe the dependence of pressure on adsorption adequately,[4] the effect of temperature on adsorption has not been explored. Knowledge of the effect of temperature on adsorption in shales is important for several reasons. First, thermal stimulation could be used if the effects of temperature on desorption are sufficiently large.[5] Second, the use of isotherms at reservoir temperatures that do not match the specific temperature for which they are used may result in poor predictions of reservoir behavior. Suitable representation of temperature effects can lead to methods for extrapolation or interpolation of measured data to reservoir conditions. Third, representations for adsorption should be adequately tested as functions of pressure and temperature if they are to be used with confidence in reservoir simulation.

In this work, we report experimental adsorption measurements for shale samples at various temperatures. We investigate the representation of adsorption behavior as a function of both temperature and pressure. We use the measured data to develop other basic thermodynamic quantities important for gas/shale adsorption.

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Modeling Adsorption

The major mineral compositions of Devonian shales are clay minerals, quartz, and organic materials, principally kerogen.[9] The amount of organic materials present in the Devonian shales differ from sample to sample, ranging from 0% to over 15%.[9] The relatively large adsorptive capacity for kerogen makes the organic material important for gas storage. **Fig. 1** shows the adsorption capacities for samples at two different pressures as a function of total organic carbon (TOC). We observed an approximately linear correlation between the adsorption capacities and TOC. This indicates that organic material is important for adsorbed gas storage. However, even samples with low TOC can have significant adsorption, indicating that other material may also be responsible for adsorption. It has long been recognized that clay minerals are capable of adsorbing significant amounts of gases and vapors.[10] The layered structure of clay minerals provides a large surface area with many adsorption sites for gas molecules. Because large quantities of clay minerals are present in shales,[9] it is likely that they also contribute significantly to the total gas storage in Devonian shales. The principal clay component is usually illite.[9] **Fig. 2** shows adsorption isotherms for illite and two shale samples measured at 77°F. The adsorptive capacity of illite is appreciable. We have investigated adsorptive properties of illite as being representative of adsorption by clays in the shales.

The Langmuir model has been used exclusively for representing Devonian shale adsorption isotherms. Indeed, we have found that it can describe the functionality of pressure at a given temperature well.[4] However, when the effects of temperature are included in the Langmuir model, we found it to be inadequate for representation of data measured at several temperatures. Consequently, we investigated alternative representations for adsorption that are consistent with the measured data. We discuss the bases for the investigated models in the following subsections.

Langmuir Model

The Langmuir model is a simplified model for monolayer gas/solid adsorption.[11] The basic assumptions of the model follow.

1. Molecules are adsorbed at a fixed number of localized sites, and one molecule at most is adsorbed on each site (monolayer adsorption).

2. All adsorption sites are energetically equivalent (homogeneous adsorbent).

3. There is no interaction between molecules adsorbed on neighboring sites.

With these assumptions, the Langmuir isotherm equation can be rigorously derived by use of thermodynamics.[11] This isotherm equation is commonly written as follows.

$$\theta = N_{ads}(p,T)/N_m = \frac{k(T)p}{1 + k(T)p}, \quad \dots\dots\dots\dots\dots\dots (1)$$

where θ is the surface coverage; $N_{ads}(p,T)$ is the amount of adsorbed gas at pressure p and temperature T per unit volume of adsorbent; N_m is the amount of adsorbed gas at monolayer coverage per unit volume of adsorbent, and $k(T)$ is the adsorption equilibrium constant, which can be taken to be temperature dependent. This constant can be expressed as[12,13]

$$k(T) = k_o T^{-\frac{1}{2}} \exp(-E/RT). \quad \dots\dots\dots\dots\dots\dots (2)$$

Here k_o is a constant independent of temperature; E is the characteristic adsorption energy, which is the difference between energies of an adsorbate molecule in the gas and adsorbed phase; and R is the universal gas constant. The Langmuir model describes monolayer
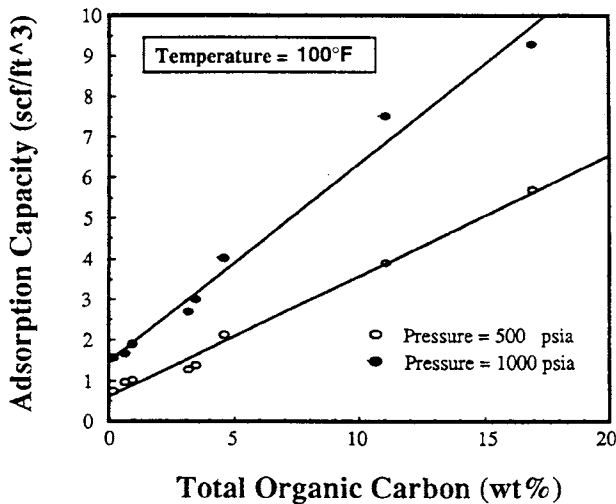
Fig. 1—Adsorption capacities and TOC for shale samples.

TABLE 1—PHYSICAL PROPERTIES OF SAMPLES				
Sample	Well Depth (ft)	Bulk Density (g/cm³)	TOC (%)	Clay (%)
Illite	—	2.576	—	—
Antrim-7	1,248	2.149	11.06	40
CSW2	3,434	2.553	0.96	38

gas adsorption on a homogeneous adsorbent having a very sharp peak of adsorption energy distribution around E (ideally, a δ-function distribution).

Bi-Langmuir Model

The assumption of homogeneous adsorbent in the Langmuir model may not be suitable for gas/shale systems because different material may contribute to gas adsorption. To extend the Langmuir model for the cases of nonhomogeneous adsorbents, various approaches have been proposed.[14] Consider an adsorbent surface having n types of adsorption sites. Let N_i denote the amount of gas adsorbed on the ith type of adsorption sites with the adsorption energy E_i. The overall amount of adsorbed gas, N_{ads}, is the sum of the amounts of adsorbed gas.

$$N_{ads} = \sum_{i=1}^{n} N_i . \quad\quad\quad\quad\quad\quad\quad (3)$$

Defining f_i as the ratio of the amount of the ith type adsorption at monolayer coverage (N_{mi}) to the total amount adsorbed at monlayer coverage (N_m), Eq. 3 can be written as

$$\frac{N_{ads}}{N_m} = \sum_{i=1}^{n}(N_i/N_{mi})(N_{mi}/N_m) = \sum_{i=1}^{n} \theta_i f_i , \quad\quad (4)$$
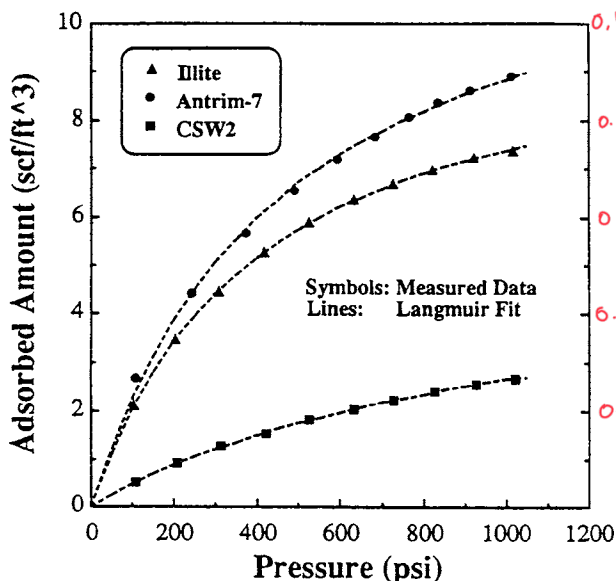
Fig. 2—Adsorption measured at 77°F with fitted Langmuir isotherms.

where θ_i is the relative coverage of the ith type adsorption site, which is assumed to follow the Langmuir equation.

As discussed previously, there is evidence that two mineral components, clay and kerogen, are the major factors responsible for condensed-phase gas storage in Devonian shales. If we regard these two components as homogeneous adsorbents, respectively, we can obtain

$$\frac{N_{ads}}{N_m} = f_1 \frac{k_1(T)p}{1 + k_1(T)p} + (1 - f_1)\frac{k_2(T)p}{1 + k_2(T)p} , \quad (5)$$

where we have used the fact that $f_1 + f_2 =$ unity. This model describes gas adsorption on an adsorbent having two discrete sharp peaks of adsorption energy distribution around E_1 and E_2 (ideally, two δ functions). One term in Eq. 5 would account for the gas adsorption on clay minerals, and the other term would account for gas adsorption on kerogen. We call this model the bi-Langmuir model. We investigate the suitability of this model and the Langmuir model to describe gas adsorption in shales below.

Procedures and Analysis

Experiments. A volumetric adsorption apparatus was designed and constructed for gas/shale adsorption measurements.[8] Accurate measurements of adsorption in shale are difficult because of the relatively small adsorptive capacities and the relatively small volumes of samples that are available. With careful attention to the experimental accuracy in design of cell volumes, temperature control, and experimental procedures, we expect the accuracy of the measured isotherm data to be within ±4% of the measured values.[8]

We used two shale samples and one illite sample in this study. The shale samples are from the Gas Research Inst.-sponsored Comprehensive Study Wells (CSW) program. The CSW2 sample is from a well in West Virginia, and the Antrim-7 sample is from a well in Michigan. We acquired the illite sample from the Clay Mineral Soc. **Table 1** lists some physical properties of the samples.[15] The TOC for Antrim-7 is much higher than that for CSW2, while the weight percentages of clay minerals are similar. The samples were crushed to 18-to 25-mesh-size particles and degassed at 120 to 140°F for 24 hours in a vacuum oven before isotherm measurement. The samples were regenerated after each measurement by evacuation at 120°F overnight. We made the isotherm measurements at four different temperatures for each sample. We used methane gas during the measurement because it is the major component of natural gas.

Parameter Estimation and Model Selection. We obtained estimates of model parameters by nonlinear regression through minimization of the performance index, J,

$$J = \sum_{i=1}^{n_i}\sum_{j=1}^{n_j}\left[N_{ads}^{E}(p_i, T_j) - N_{ads}^{C}(p_i, T_j)\right]^2 , \quad (6)$$

where $N_{ads}^{E}(p_i, T_j)$ is the amount adsorbed measured at pressure p_i and temperature T_j and $N_{ads}^{C}(p_i, T_j)$ is calculated by either the Langmuir equation (Eq. 1) or the bi-Langmuir equation (Eq. 5). Three parameters are estimated in the Langmuir model and six parameters in the bi-Langmuir model. We used 40 data for each sample, corresponding to 10 values measured at each of four temperatures.

Once we estimated the parameters in the models, we used a statistical test (the F test[16]) to determine the more appropriate representation. We performed the F test by comparing a tabulated value with a statistic calculated with values of the sum of squared residuals S corresponding to the more complete model with a simpler, nested model. The calculated statistic is

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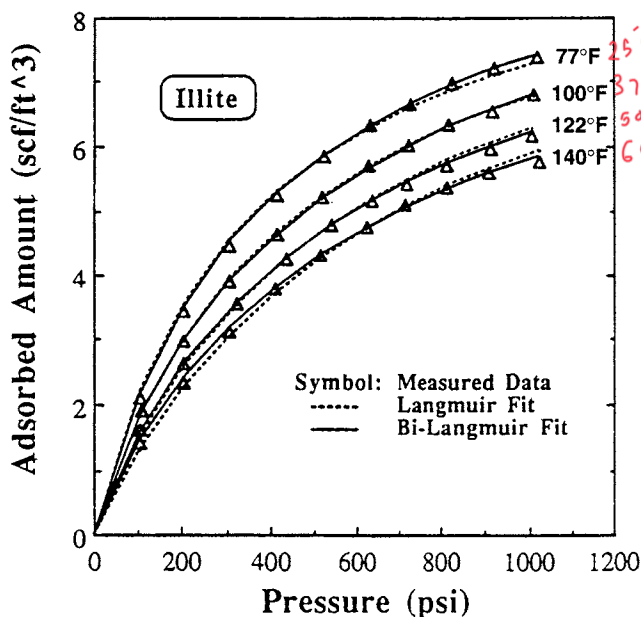
Fig. 3—Measured adsorption with fitted models for illite sample.

$$F = \frac{[S_{\text{sim}} - S_{\text{com}}]/d}{S_{\text{com}}/\left(n_i n_j - q\right)} , \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

where the subscripts sim and com stand for simpler model and more complete models, respectively, d is the difference of number of parameters of the two models, $n_i n_j$ is the number of observed data points, and q is the number of parameters of the more complete model. If the tabulated value exceeds the calculated statistic, one concludes (at the specified level of significance) that the available data do not warrant inclusion of the additional terms in the complete model. For nonlinear regression, the confidence level is approximate.[17]

Results and Discussion

Model Studies. Fig. 2 shows the measured amounts of methane adsorbed at 77°F for the illite, Antrim-7, and CSW2 samples together with the fitted Langmuir models. It can be seen that the adsorption
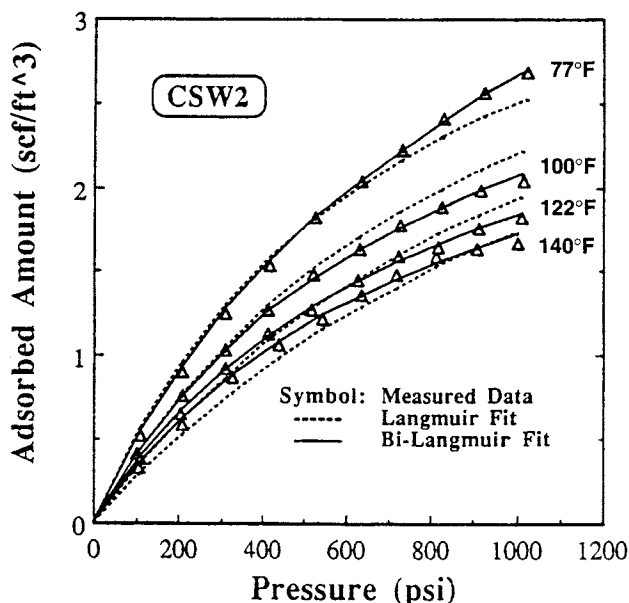

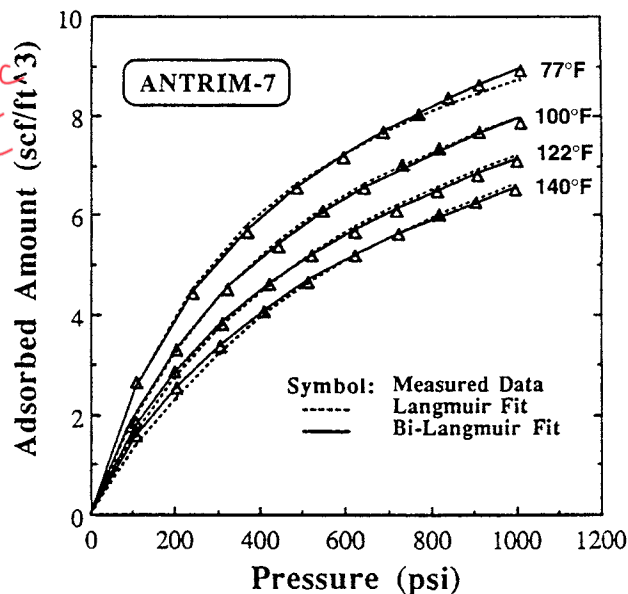Fig. 5—Measured adsorption with fitted models for CSW2 Sample.

Fig. 4—Measured adsorption with fitted models for Antrim-7 sample.

capacity of sample Antrim-7 is much larger than that of the sample CSW2. This is attributed to the larger organic content present in sample Antrim-7 compared with that in sample CSW2 (see Table 1). As Fig. 2 shows, the Langmuir model provides a reasonably good fit for adsorption data measured at a single temperature.

Figs. 3 through 5 show the measured amounts of methane adsorbed on the samples at temperatures of 77, 100, 122, and 140°F. The values corresponding to the fitted Langmuir and bi-Langmuir models are shown in the figures as dashed lines and solid lines, respectively. **Tables 2 and 3** list the parameter estimates and the F test results, respectively. As can be seen from the figures, the bi-Langmuir model provides a more precise representation of the data for each sample and an adequate representation for all the samples. The Langmuir model clearly failed as a representation for the CSW2 sample (Fig. 5). The F-test results in Table 3 support the selection of the bi-Langmuir model as the more appropriate representation for each sample.

The better representation of adsorption by the bi-Langmuir model for the Antrim-7 and CSW2 samples is consistent with our observation that two mineral sites are important for adsorption. The better representation of the bi-Langmuir model for illite may be attributed to impurities or variations in structure that may be present in the illite sample.

Although we did not study the effect of model selection on production forecasts, the following observations regarding implications for field study can be made. Because the Langmuir isotherm is capable of representing fairly well the pressure functionality at a given temperature, a Langmuir equation is expected to be sufficient whenever measured adsorption data are available for the range of pressures and the temperatures for which they are required for simulation. The use of the bi-Langmuir model would likely be important whenever estimates of the isotherms are desired at temperatures for which there are no measured data. Note that at the higher pressures, the Langmuir model underpredicts the sensitivity of temperature for each of the samples (Figs. 3 through 5). That is, the difference between the data at the smallest and largest temperatures is always more than that predicted by the Langmuir model. To get some idea of the importance of the model selection in extrapolation of temperature, we calculated the isotherms at 176°F for CSW2 using both models. Even though the extrapolation temperature is not that far outside the range of the data, the predictions differ significantly (see **Fig. 6**). This demonstrates that care should be taken in representing temperature effects on adsorption.

TABLE 2—ESTIMATES OF PARAMETERS OF LANGMUIR AND BI-LANGMUIR MODELS

Langmuir Model

Sample	N_m (scf/ft^3)	k_o (1/psi)	$-E$ (kcal/mol)	R^2	S
Illite	9.93	1.96×10^{-4}	3.25	0.998	0.186
Antrim-7	12.36	7.42×10^{-5}	3.74	0.997	0.396
CSW2	4.32	4.31×10^{-5}	3.74	0.984	0.223

Bi-Langmuir Model

Sample	N_m (scf/ft^3)	k_{o1} (1/psi)	k_{o2} (1/psi)	$-E_1$ (kcal/mol)	$-E_2$ (kcal/mol)	f_1	R^2	S
Illite	10.42	4.80×10^{-3}	5.99×10^{-8}	1.39	7.78	0.68	1.000	0.040
Antrim-7	15.08	9.65×10^{-4}	7.42×10^{-6}	2.49	4.82	0.42	1.000	0.074
CSW2	26.10	2.89×10^{-3}	6.29×10^{-15}	1.35	14.98	0.12	0.999	0.017

TABLE 3—F TEST FOR LANGMUIR AND BI-LANGMUIR MODELS

Sample	F	$F_{d,nm-q}^{0.99}$
Illite	41.37	4.51
Antrim-7	49.31	4.51
CSW2	144.00	4.51

Isoteric Heats of Adsorption

The gas/shale adsorption energy is required to calculate the energy requirements for the thermal stimulations of shale gas wells. The isosteric heat of adsorption, q^{st}, which is the adsorption energy at a specified surface coverage, can be calculated with the model-independent Clausius-Clapeyron phase equilibrium equation,[11]

$$q^{st} = -R\left[\frac{\Delta \ln p}{\Delta(1/T)}\right]_{N_{ads}} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (8)$$

By plotting the logarithms of adsorption pressure vs. reciprocals of isotherm temperature, we can obtain a straight line (q^{st} is usually independent of temperature), and we can calculate the isosteric heat, q^{st}, at a specified N_{ads} value from the slope of the straight line. We used adsorption isotherms measured at four different temperatures for isosteric heat calculations for the illite, Antrim-7, and CSW2 samples.

Fig. 7 is a plot of the isosteric heat vs. surface coverage. As shown in the figure, all the isosteric heats of adsorption are higher than the latent heat of methane condensation. This is expected because methane is a supercritical gas at the experimental conditions and capillary condensation will not take place. The isosteric heats of adsorption for three samples follow the same trend; i.e., there is an initial decrease of isosteric heat at low coverages and a gradual increase at higher coverages. It is generally recognized[18] that the heterogeneity of the adsorbent causes the initial decrease of the isosteric heat because the adsorption occurs first on the sites with the highest adsorption energy. The gradual increase of isosteric heat at higher coverages may be caused by the molecular interactions among the adsorbed molecules,[18] as such interactions get stronger when more gas molecules are adsorbed. Fig. 7 also shows that the variations of isosteric heats for different samples at various coverages are relatively small, ranging from 2.6 to 4.2 kcal/mol. The isosteric heat for the Antrim-7 sample, which is the sample with large organic content, is larger than that of the other samples, indicating the adsorption heats on kerogen may be larger than those on illite and other clay minerals.

Conclusions

The amount of natural gas existing as an adsorbed or condensed phase in Devonian shales depends on temperature as well as pressure. It is important to know this relationship to make reliable predictions of reservoir behavior. Temperature dependence has not been explored previously.

We used adsorption measurements at various temperatures to investigate the representation of gas adsorption as a function of temperature and pressure and to determine the isosteric heats of adsorp-
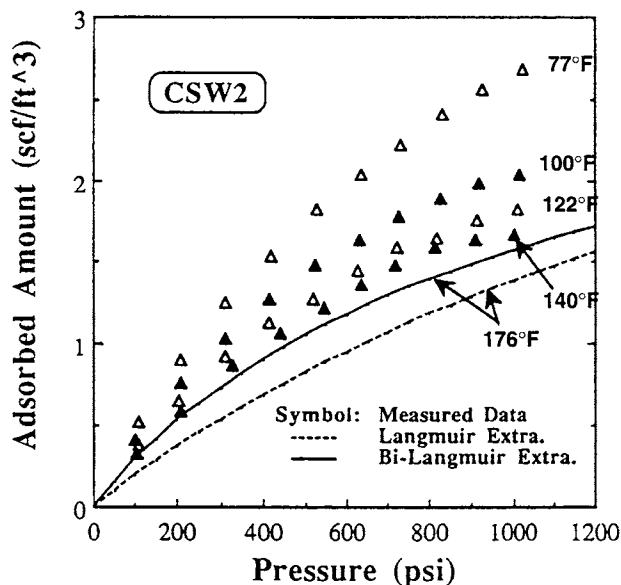

Fig. 6—Extrapolated isotherms with measured adsorption for CSW2 Sample.
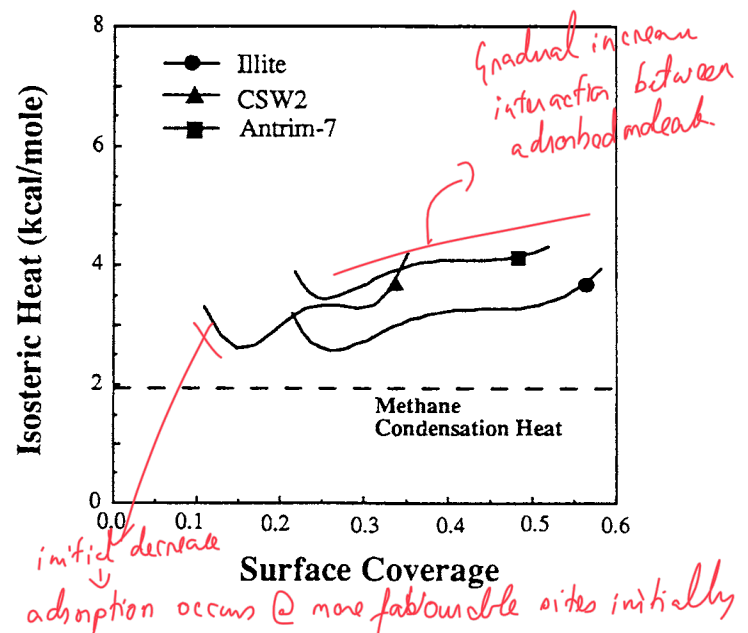

Fig. 7—Isoteric heats for illite, Antrim-7, and CSW2 samples.

tion. Although the Langmuir model can adequately represent gas/shale isotherms measured at a single temperature, it is not adequate for representation of multiple temperatures. The bi-Langmuir model was able to represent the effects of pressure and temperature for the samples studied. Accurate representation of temperature effects is particularly important for consideration of thermal recovery methods or for extrapolation of laboratory measurements to reservoir conditions.

Nomenclature

$d =$ difference in numbers of parameters
$E =$ adsorption energy, mL^2/t^2, kcal/mol
$f =$ fraction of adsorption site
$F = F$ statistic
$J =$ performance index
$k =$ adsorption equilibrium constant, Lt^2/m, 1/psi
$n =$ number of types of adsorption sites
$n_i =$ number of pressure values
$n_j =$ number of temperature values
$N =$ amount of adsorbed gas per unit volume adsorbent, L^3/L^3, scf/ft^3
$p =$ pressure, m/Lt^2, psi
$q^{st} =$ isosteric heat, mL^2/t^2, kcal/mol
$R =$ universal gas constant, mL^2/t^2T, kcal/(mol°R)
$S =$ sum of squared residuals
$T =$ temperature, T, °F
$\theta =$ surface coverage

Superscripts

$C =$ calculated data
$E =$ experimental data

Subscripts

$ads =$ adsorption
$m =$ adsorption at monolayer coverage
$mi =$ adsorption of ith type at monolayer coverage

Acknowledgments

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SI Metric Conversion Factors

ft × 3.048*	E − 01	= m
ft^3 × 2.831 685	E − 02	= m^3
°F (°F−32)/1.8		= °C
in.^{3} × 1.638 706	E + 01	= cm^3
kcal/g mol × 4.184*	C + 03	= kJ/kmol
psi × 6.894 757	E + 00	= kPa

*Conversion factor is exact.   **SPEFE**

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