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Selective adsorption of hydrocarbon gases on clays and organic matter

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Abstract

The adsorption selectivity for C_1–C_6 hydrocarbons in a gas mixture on a variety of adsorbents was measured at 26 and 80 °C at total pressures of 1, 2 and 3 atm. The adsorption isotherm reveals that the adsorption levels are higher for organic matter than for clays, although the selectivity is similar. Coal adsorbs gases more than oil shale, kaolinite adsorbs less total gases but more methane than montmorillonite whereas activated carbon shows much stronger adsorption capacity than the other studied samples. The proportion of the adsorptive amount relative to the initial amount for each gas component at steady state condition increases with decreasing their vapor pressures (p_o) (from C_1 to C_6). The normalized adsorptive amount for each adsorbed gas increases with increasing partial pressures (p_i) of the gas in the system. The trends, in the case of oil shale, follow nearly a single trend curve as the adsorption level was plotted against relative pressure (p_i/p_o). This confirms that the adsorption selectivity is mainly caused by variations in the vapor pressure of the gases. In addition, the measured adsorption rates of gases on the studied adsorbents can be reasonably described using the Elovich kinetic model.

1. Introduction

The composition of reservoir hydrocarbon gas is generally significantly different from that predicted by experimental simulation of the gas generation from its inferred source rocks (Mango, 1992; Snowdon, 2001; Behar and Vandenbroucke, 1996). In particular, the methane fraction in the gases generated during artificial maturation is usually lower than that observed in actual petroleum reservoirs (e.g. 85±15% of methane; Mango, 1996). Based on the study of gas from cuttings, Snowdon (2001) suggests that the composition of gas generated in geological environments is much wetter (20±10% of methane). The compositional difference between generated and accumulated gases is attributed mainly to various geological processes. The difference of organic matter types and maturity (Behar and Vandenbroucke, 1996; Hunt, 1995), and compositional fractionations during primary and secondary migration are believed to be major causes for the observed differences (Price and Schoell, 1995). These include well known geological processes, such as the mixing with biogenic gas in nature (e.g. Hunt, 1995), formation and decomposition of gas hydrate (Snowdon, 2001), evaporative fractionation through vertical migration (Thompson, 1987, 1988; Snowdon, 2001), and bio-degradation and secondary cracking of oils (Behar et al., 1991, 1995; Behar and Vandenbroucke, 1996). Other less-understood processes include the preferential retention of wet hydrocarbon gases in coal, organic matter, clays and other geological materials during primary and secondary migration.

The adsorption of hydrocarbon gases on coals has been reported by many previous studies (Crosdale, 1998; Siahaan, 1990; Crosdale et al., 1998; Smith and Williams, 1987; Ting, 1987; Ettinger, 1984). Most of these studies, however, focus mainly on methane

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adsorption in the coal bed. For instance, methane adsorption capacity on coals has been experimentally measured at pressures and temperatures close to reservoir conditions (Gaschnitz et al., 1997; Clarkson and Bustin, 1996). Few studies, however, have measured adsorption capacities of wet gases and their adsorption selectivity relative to methane on coals (Kreamer et al., 1994; Rodriguez et al., 1997; Melnitchenko et al., 2000). For other geological materials such as clays, most studies have focused on the adsorption study of polar organic compounds (Bissada and John, 1969; Berrada, 1992; Goss, 1994) or volatile organic compounds (Goss, 1996; Morrissey and Grismer, 1999; Donahue et al., 1999). Studies of adsorption of methane and wet hydrocarbon gases on clays are less reported because it is believed that mineral matter is essentially non-adsorptive to methane (Crosdale et al., 1998; Stoessell and Byrne, 1982; Kosuge, 1994), although the adsorption of methane, ethane on crystalline silica (Choudhary and Mayadevi, 1996) and non-hydrocarbon gases including noble gases has been measured in clay systems (Aylmore, 1974).

This study presents experimental data on the adsorption selectivity of hydrocarbon gases on clays and organic matter in a simple system. The application of results from the simple system is limited since the experiments were conducted at dry condition and low pressure. In reality, gas retention and migration proceed in the presence of fluid phases (formation water and oil) while the adsorption occurs at gas-solid and liquid-solid interfaces or possibly in a three-phase system at higher subsurface pressures. The results from the simple system, however, may provide basic information for future experiments in a complex system close to natural conditions involving retention and fractionation of the migrated hydrocarbon gases.

2. Experimental procedures

2.1. General remarks

The measurement of the adsorption capacities of gases on solid matter has been previously done using a variety of methods, including thermogravimetric analysis (TGA). This study used an analytical method, which measures the compositional change of gas before and after the adsorption, and calculates the adsorption capacities and selectivity using mass balance.

2.2. Starting materials

The hydrocarbon gas mixture used as adsorbate was HP Petrochemical Standards (4 l, at 60 psi, 21 °C; Scott Specialty Gas inc.), containing methane volume 69%, ethane 9%, propane 6%, *n*-butane 3%, *i*-butane 3%, *n*-pentane1%, *i*-pentane 1%, hexane 0.5%, nitrogen 6%, carbon dioxide 1%, oxygen, 0.5%.

The adsorbents used included kaolinite, Na-montmorillonite, humic coal, and oil shale. Two other synthetic samples, granular corundum (boiling stone), and activated carbon, which, respectively, represent materials with low and very high adsorption capacity, were also used as reference. The specific surface areas of these samples were measured by NOVA 2000™ using the BET method. Kaolinite is KGa-1b CMS reference clay sample from Clay Mineral Society (CMS) Source Clay Minerals Repository. The specific surface area (10.05 m^2/g) measured by BET method was slightly less than that (11.98 m^2/g) previously reported (Olphen and Fripiat, 1979). Na-saturated montmorillonite clays were from the reference clay sample (Swy-2 from CMS) which was treated by the conventional Na-exchanged method. The specific surface area measured by BET method is 31.78 m^2/g, which is similar to that previously reported for Swy-1 (Olphen and Fripiat, 1979).

The humic coal used was a shaly coal sample from Taiwan, and the oil shale sample was from Green River Formation, Utah, USA. The sample pyrolyzed using Rock-Eval 6 apparatus showed a hydrogen index (HI) = 327 mg HC/g of TOC and TOC 24.7% for the shaly coal and an HI of 790 mg HC/g TOC and TOC of 20.2% for the oil shale. The sample particles of the shaly coal and oil shale used for adsorption experiments were less than 70 mesh (0.21 mm). The specific surface areas measured using BET method, were 1.19 m^2/g and 2.19 m^2/g, respectively, for the shaly coal and oil shale.

The activated carbon and granular corundum (boiling stones) were commercial, synthetic samples. The average grain size of the activated carbon and boiling stone, respectively, were 1.8 mm and 2.8 mm in diameter; the densities were, respectively, 0.475 and 2.82 g/cm^3, and the specific surface areas measured by the BET method were, respectively, 1020.4 m^2/g and 0.88 m^2/g.

2.3. Experimental apparatus and procedures

The apparatus used for adsorption experiments was a sealed stainless cylinder (13 cm height, 6 cm I.D., Fig. 1) with a sample chamber of 175.4 cm^3. The space of the sample chamber can vary by inserting a solid cylinder of different sizes to reduce the sample chamber to the desired volume. The chamber volume used in the present experiments was 43.85 cm^3. The free gas volume was corrected by subtracting the solid sample volume from the chamber volume. The apparatus is equipped with a pressure sensor connected to a digital pressure gauge to measure the gas pressure within the sample chamber. A window with a septum was designed on the top of the cylinder for injecting starting gas into the sample chamber or withdrawing gas from the chamber during an experiment for compositional analysis.

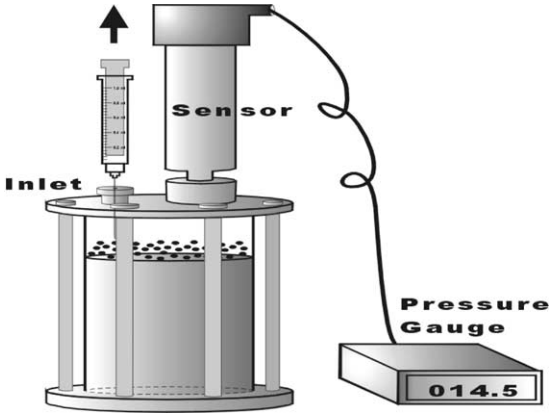

Fig. 1. Experimental set up for adsorption experiments, including a pressure chamber, an inlet or outlet septum, and pressure sensor with gauge.

The amount and composition of the gas sample were analyzed using an FID equipped HP6890 gas-chromatograph (GC). The capillary column had 0.53 mm I.D. and 15 m length (HP-Plot Al_2O_3). Chromatographic grade (99.9995%) helium gas was used as carrier gas. The inlet and detector temperatures, respectively, were both 250 °C, whereas the oven was programmed at 100 °C for 1.5 min, then at 30 °C/min to 180 °C, and isothermal for 1 min. The calibration curves for hydrocarbon gas components (C_1–C_6) were made frequently to quantify the absolute amount of each gas component.

The desired amounts of starting sample powder were dried at 110 °C for 20 min immediately before loading into the sample chamber. The sample chamber was then sealed and evacuated to a pressure of about 10^{-2} torr. The starting gas was first transferred into a separated steel cylinder equipped with a pressure sensor/gauge and a septum. Starting gas of known volume and pressure was transferred to the sample chamber from the steel cylinder using a 5 ml gas-tight syringe. The amounts of gas extracted were calculated from the gas pressure and volume in the syringe using equation of state for perfect gas. The extracted gas was then injected into the evacuated sample chamber. It took a total of about 5 to 10 min to repeat this procedure until the desired gas pressure in the sample chamber was reached. The total amounts of initial gas in the sample chamber (Table 1) before the onset of adsorption were calculated by summing up the amounts of gas repeatedly extracted. The small amount of initial adsorption during the injection period does not affect the measured adsorption capacity but may cause uncertainty for determining time-zero used for kinetic modeling. The experimental results show that the uncertainty is not significant except for activated carbon, on which a significant amount of gases were adsorbed during the injection period. For each gas analysis, 0.1 ml of gas was sampled at intervals of 5–6 min during the first hour and 20 min or longer after the first hour using a 1 ml gas-tight syringe through the septum. After each sampling, the gas was injected into the inlet of the gas chromatograph for compositional analysis.

The amounts and the composition of the adsorbed gases were calculated by mass balance from those of the un-adsorbed free gas, which were analyzed in the experiments. In order to eliminate the uncertainty caused by the variation of gas volume (0.1 ± 0.005 ml) injected into the GC, the mass ratio of each pair of gas components (e.g. Cx/C_1, Cx/C_2 etc.), instead of absolute amounts in the free space, was measured. In order to calculate adsorption levels near saturation, most experiments were extended until the ratios between any two gas components reached steady state. The adsorbed amount for each component (Table 1) was then calculated by

Table 1
Experimental data for the adsorption capacities of hydrocarbon gases at steady-state condition

	Activated carbon		Shaly coal		Green River shale		Montmorillonite		Kaolinite		Boiling stone	
	Initial	Adsorbed	Initial	Adsorbed	Initial	Adsorbed	Initial	Adsorbed	Initial	Adsorbed	Initial	Adsorbed
C_1	4.39	3.45	1.21	0.151	1.17	0.0492	1.18	0.0466	1.49	0.121	1.27	0.0036
C_2	0.573	0.563	0.157	0.0353	0.152	0.0364	0.154	0.0299	0.194	0.0303	0.166	0.0166
C_3	0.382	0.381	0.105	0.0572	0.101	0.0524	0.103	0.0371	0.129	0.0352	0.111	0.0321
i-C_4	0.191	0.191	0.0525	0.0313	0.0507	0.0337	0.0513	0.0222	0.0646	0.0214	0.0553	0.02
n-C_4	0.191	0.191	0.0525	0.0424	0.0507	0.0403	0.0513	0.033	0.0646	0.0301	0.0553	0.0328
i-C_5	0.0636	0.0636	0.0175	0.0149	0.0169	0.0149	0.0171	0.0124	0.0215	0.0122	0.0184	0.0129
n-C_5	0.0636	0.0636	0.0175	0.0163	0.0169	0.0157	0.0171	0.0147	0.0215	0.0149	0.0184	0.0159
C_6	0.0318	0.0318	0.00875	0.0085	0.00845	0.0083	0.00855	0.0081	0.0108	0.0092	0.00922	0.0089
Sum mmol/10g	5.886	4.935	1.62075	0.3569	1.56665	0.2509	1.58235	0.204	1.996	0.2743	1.70362	0.1428

Note: Amounts of individual hydrocarbon in milli-moles per 10 gram of adsorbent. "Initial" indicates the initial amount of each gas component injected into the sample chamber. "Adsorbed" indicates the amount of each gas component adsorbed on the adsorbent at steady-state condition near saturation. Adsorption experiments were carried out at 26 °C and about 1 atm.

Table 2
Comparison of adsorption capacities of hydrocarbon gases on the studied adsorbents

	Initial*	Activated carbon	Coal layer	Green River shale	Montmorillonite	Kaolinite	Boiling stone
C_1	4.39	3.45	0.55	0.19	0.17	0.35	0.01
C_2	0.57	0.56	0.13	0.14	0.11	0.09	0.06
C_3	0.38	0.38	0.21	0.20	0.14	0.10	0.11
i-C_4	0.19	0.19	0.11	0.13	0.08	0.06	0.07
n-C_4	0.19	0.19	0.15	0.15	0.12	0.09	0.11
i-C_5	0.06	0.06	0.05	0.06	0.05	0.04	0.04
n-C_5	0.06	0.06	0.06	0.06	0.05	0.04	0.05
C_6	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Sum (mmol/10g)	5.89	4.94	1.30	0.94	0.76	0.60	0.49

* Initial amounts of gases used for experiments with different adsorbents were different. For comparison, the adsorption capacities shown in Table 1 were recalculated in this table to the same initial amounts of gas as used for the activated carbon experiment.

averaging the Cx values obtained from different ratios. Note that the total amounts of natural gases (adsorbed + un-adsorbed) in the chamber used for the calculation decrease slightly during the sampling and have been corrected after each sampling.

3. Experimental results and discussions

3.1. Absorption capacity and selectivity

It has been shown that the adsorption capacity and selectivity of the studied adsorbents for the hydrocarbon gas mixture measured at equilibrium (or steady-state) are significantly different (Table 1). The comparison of the adsorption capacities for different adsorbents is hard to make because the initial amounts of gases used for experiments with different adsorbents were different. For better comparison, the adsorption capacities have been recalculated to the same initial amounts of gases as those used for the activated carbon. Activated carbon, as expected, adsorbs the most; the geological samples, shaly coal, oil shale, montmorillonite, and kaolinite, adsorb hydrocarbon gases at levels much less than the activated carbon (Table 2; Fig. 2). The adsorption isotherms indicate that the adsorption capacities of total hydrocarbon gases on these geological materials decrease successively in the order of the above sequence. This order, however, is not consistent with the surface areas of the samples, and, therefore cannot be interpreted simply by surface adsorption. Organic matter with lower surface areas adsorbs hydrocarbon gases much more than the higher surface-area clays, implying the likelihood of other retention capabilities, such as absorption (Ettinger and Serpinsky, 1991) or pore-filling (Crosdale, 1998) of gases in the organic matter samples. The gas retention capacity per gram of organic matter is greater for the coal than for the oil shale, implying that the capacity of Type III organic matter, in general, is probably greater than that for Type I organic matter. This speculation is reasonable because Type III organic matter has a higher gas generative capability than Type I and, therefore, very likely has higher adsorption (Mukhopadhyay et al., 1997). This confirms the previous observations from the study of coalbed methane, that coals can store large quantities of gases. It is shown that montmorillonite adsorbs these gases at unexpectedly low levels, only slightly higher than kaolinite, with a difference lower than that expected from the difference in external surface areas of these two clays. It appears that the larger internal surface area of montmorillonite does not significantly increase its adsorption capacity of hydrocarbon gases under these experimental conditions. Kaolinite adsorbs more methane than oil shale and montmorillonite although it has less adsorption capacity for total gas.

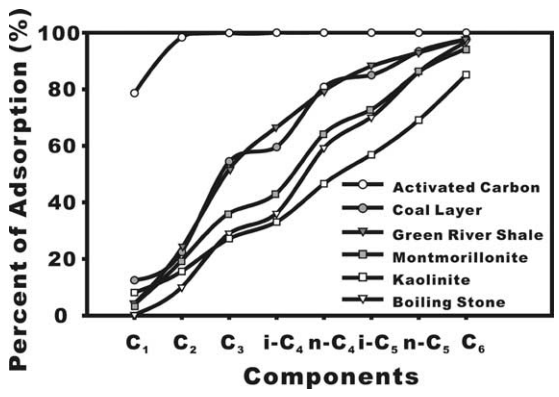

Fig. 2. Selective adsorption capacities of different hydrocarbon gases on the studied adsorbents near saturation (or steady-state) measured at 1 atm total pressure and 26 °C. Percent adsorption is the adsorptive amounts relative to its original concentration in the initial gas mixture. Abbreviations: C_1 = methane; C_2 = ethane, C_3 = propane, *i*-C_4 = *iso*-butane; *n*-C_4 = normal butane; *i*-C_5 = *iso*-pentane; *n*-C_5 = normal pentane; C_6 = hexane.

Large adsorption selectivity of hydrocarbon gas molecules (C_1–C_6) has been observed (Fig. 2). Gases with higher molecular weight or boiling points are preferentially adsorbed on all the studied samples. The percentages of adsorption for each component relative to its initial amount in the gas mixtures were compared and are presented in Fig. 2, which shows a dramatic increase with increasing carbon number of the adsorbed gases. For each hydrocarbon component, the percent of adsorption varies with the adsorbents used; for example, the adsorption of methane on the studied samples ranges, for clays, from 4 to 8.1 mol%, while for coal sample is 12.5 mol%, while adsorption of propane is between 60 and 80 mol% for clays, reaching 93 mol% for coal. Note that the adsorptive capacity of activated carbon is so high that 78.6 mol% of methane and near 100% of other components were adsorbed. This near complete adsorption indicates that the adsorption sites of activated carbon were, beside methane, not saturated for hydrocarbon gases.

Fig. 3 attempts to correlate the variations of adsorptive capacity and selectivity with the surface areas of the samples in terms of the adsorptive capacity per unit surface area. Among all studied samples gas is adsorbed most on unit surface area of the coal but least on unit surface of the activated carbon. To explain this behavior, a simple calculation was made to estimate the total coverage areas of each hydrocarbon component assuming that all adsorbed molecules were closely packed in one layer. The area covered by each molecule is assumed and calculated based on the diameters of the hydrocarbon molecules. The covered areas for methane molecule on activated carbon, coal, shale, montmorillonite, kaolinite and boiling stone are 23.5, 1.03, 0.33, 0.32, 0.82 and 0.02 m^2 per gram of adsorbent, respectively, whereas, the total areas for all hydrocarbon molecules in one layer are, respectively, 41, 3.7, 2.9, 2.3, 2.8 and 1.9 m^2/g. The covered area when compared with

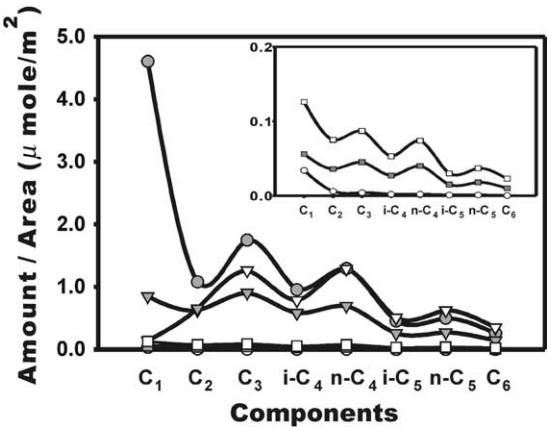

Fig. 3. Adsorptive capacity of hydrocarbon gases per unit surface area of adsorbents near saturation (or steady-state) measured at 1 atm total pressure and 26 °C. Abbreviations: open circles = activated carbon; solid circles = coal; solid triangle = Green River shale; solid squares = montmorillonite; open square = kaolinite; open triangle = boiling stone. The inset represents the enlargement of the scale in the vertical axis ranging from 0 to 0.2 μmol/m^2 for kaolinite, montmorillonite, and activated carbon.

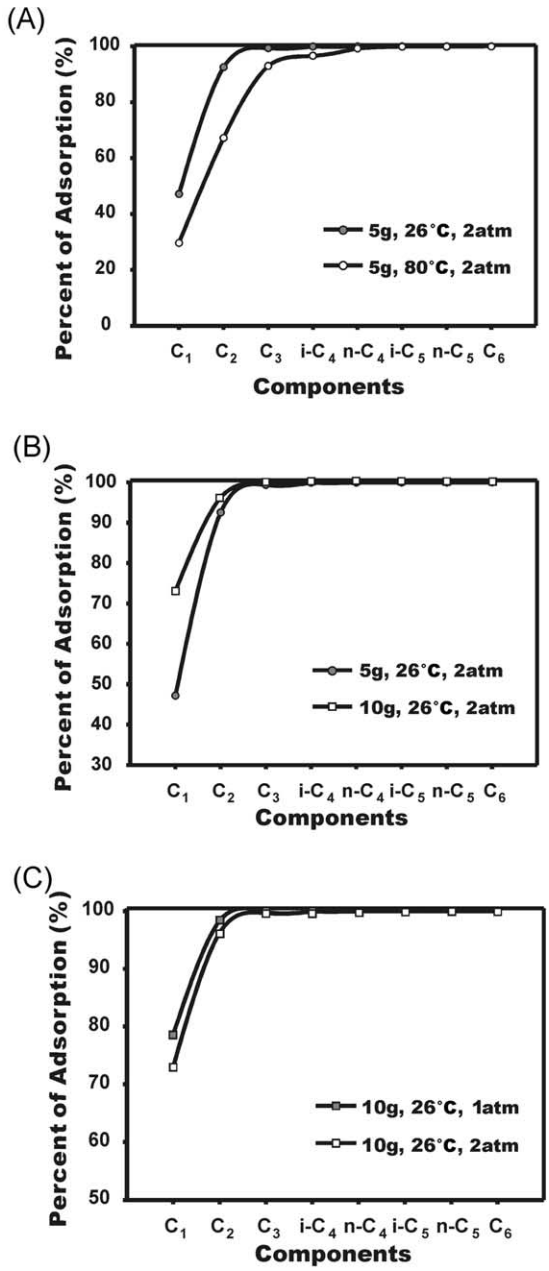

Fig. 4. The percent of the adsorption of different hydrocarbon gases on activated carbon as functions of (A) temperatures, (B) the amount of adsorbents, and (C) total gas pressure. For symbols of hydrocarbons see caption in Fig. 2. Percent of adsorption was defined in Fig. 2.

the specific surface areas of the adsorbents provides information about the percent of coverage or the numbers of layers on the adsorbents if we assume a simple surface area adsorption. The covered area of organic matter (307.3% for shaly coal and 133% for oil shale) is much higher than that for clays (7.6% for montmorillonite, and 23.3% for kaolinite). This high coverage of the organic matter, which indicated more than one layer coverage, suggests that additional retention mechanisms, such as absorption, contribute significantly. For non-geological samples, the low percent of total coverage (4%) on activated carbon is somewhat surprising. It is likely that most of its surface area was preferentially covered by nitrogen and carbon dioxide gases present in the starting gas sample. Some micropores of activated carbon may be too small for methane to diffuse into because the molecular size of methane (3.8 Å diameter) is larger than N_2 (2.8 Å) and CO_2 (3.6 Å). The latter two more readily diffuse into its pore structure. The reason for the high coverage in boiling stones (213%) relative to its surface area, is not clear.

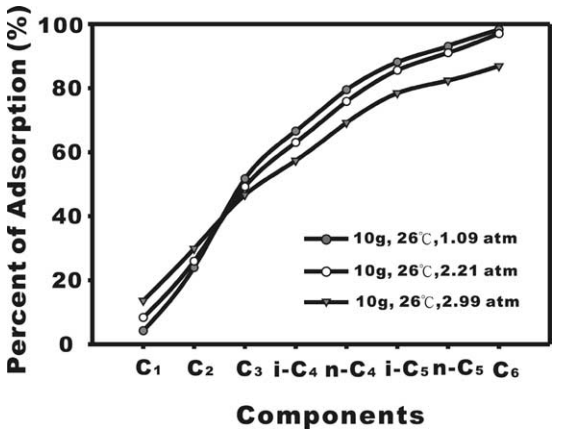

Fig. 5. Effects of total gas pressure on the percent of the adsorption using 10 grams of Green River shale as the adsorbent at 26 °C and three different pressures: 1.09 atm (110.4 kPa), 2.21 atm (223.9 kPa), and 2.99 atm (303.2 kPa). Percent of adsorption was defined in Fig. 2.

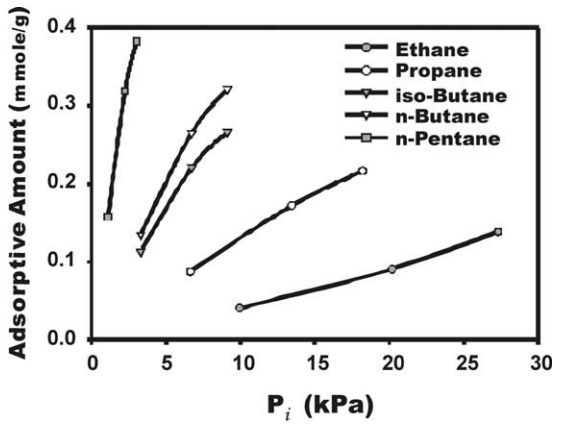

Fig. 6. The normalized adsorptive amounts of C2 to C6 hydrocarbon gases correlated to their partial pressures (p_i) in the initial gas mixture. Adsorptive amounts of different gases were normalized to the same level as the total gas amount, that is, by dividing the actual adsorptive amount of each gas by the mole fraction of the gas in the starting mixture. The adsorbent is Green River shale while the temperature is 26 °C and the total gas pressures are 1.09 atm (110.4 kPa), 2.21 atm (223.9 kPa), and 2.99 atm (303.2 kPa).

3.2. Effect of temperature and pressure on the adsorptive capacity and selectivity

The adsorption capacity and selectivity of gases on activated carbon have been studied as a function of

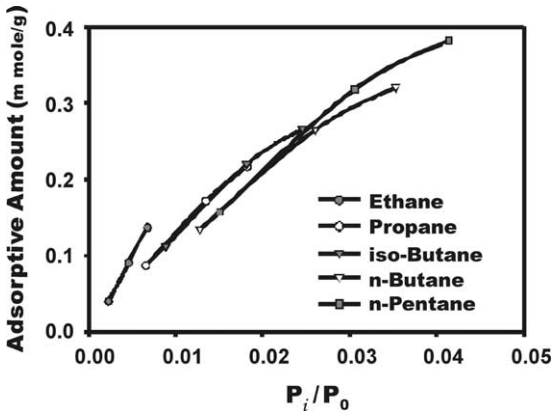

Fig. 7. Normalized adsorptive amounts of C2–C6 hydrocarbon gases as related to their relative pressures (p_i/p_o) in the initial gas mixture. Normalized adsorptive amount was defined in Fig. 6. The adsorbent is Green River shale while the temperature is 26 °C and the total gas pressures are 1.09 atm (110.4 kPa), 2.21 atm (223.9 kPa), and 2.99 atm (303.2 kPa).

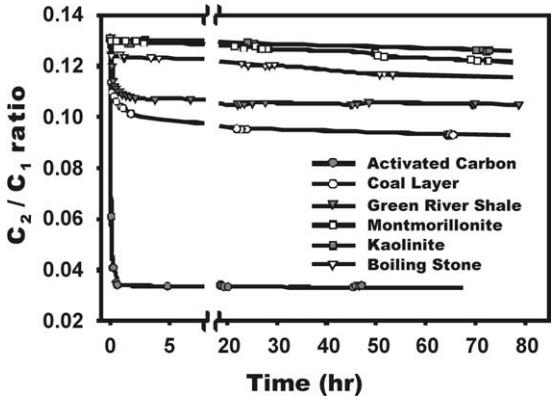

Fig. 8. The decrease of ethane/methane ratio in the gas phase as a function of time during an adsorption experiment with different adsorbents at 26 °C and 1 atm.

temperature and pressure. Our results show that at 2 atm total gas-pressure, the adsorption capacity of each component in terms of the percent of adsorption relative to its initial amount for C_1 to C_4 decreases significantly as the temperature increases from 26 to 80 °C (Fig. 4A). The effect of temperature cannot be evaluated for C_5 and C_6 because full or total adsorption has been reached very fast (Fig. 4A). The percent of hydrocarbon gases adsorbed on activated carbon appears to decrease with increasing pressure, although the difference is small. The effect of increasing pressure from 1 to 2 atm at 26 °C appears less significant (Fig. 4C). The difference also can be within the experimental uncertainty. The results also show that an increase of the amount of activated carbon from 5 grams to 10 grams increases the percent of adsorptive gases (Fig. 4B). Similar experiments for the Green River shale sample at 1.1, 2.2, and 3 atm show a significant pressure effect on the adsorption capacity and selectivity. The results indicate that with increasing total pressure, the percent of adsorption of individual gas relative to its initial amount increases for C_1 and C_2 but decreases for C_4, C_5 and C_6 gases with only a very small pressure effect for C_3 gas (Fig. 5). The pressure effect for C_1 and C_2 is inconsistent with that observed for activated carbon. The reason for the reverse of the pressure effect is not clear.

The adsorption capacity of hydrocarbon gases on the Green River shale has been correlated with their partial pressure. The adsorption capacity was re-calculated by normalizing the adsorptive amount to the total amount of original gas mixture, by dividing the actual adsorptive amount of each gas by the mole fraction of the gas in the mixture. The results (Fig. 6) show that the normalized adsorptive amount of each gas component successively increases with increasing its partial pressure in the gas mixture, and that the normalized adsorptive

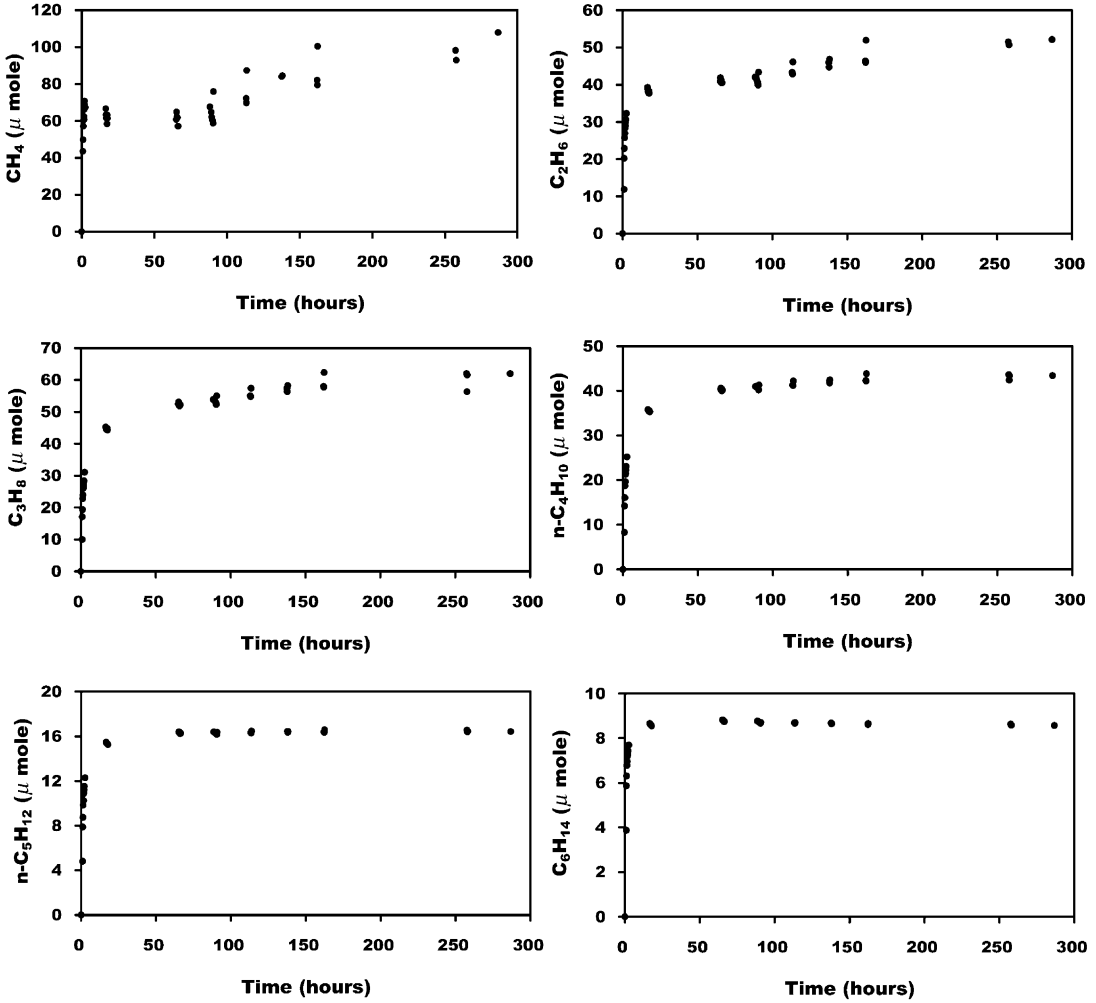

Fig. 9. The amounts of hydrocarbon gases adsorbed on 10 g of shaly coal as a function of time. The solid circles are experimental data at 26 °C and 1 atm.

amount of different hydrocarbon gases increases successively with increasing their molecular weight or decreasing their saturated vapor pressures, p_o. This is also supported by the higher adsorption capacity of *i*-C_4 than *n*-C_4 since *i*-C_4 has higher p_o, which confirms that the adsorption selectivity of hydrocarbon gases is closely related to their molecule weights or related properties, such as vapor pressure, molecule size etc.

The effect of pressure of hydrocarbon gases on their selectivity was further examined by presenting the adsorption isotherms on a plot of normalized adsorptive amounts vs. relative pressure (p_i/p_o). The adsorption isotherms show that the adsorption capacities for different hydrocarbon gases are similar at the same relative pressure (Fig. 7). This implies that the observed selectivity of hydrocarbon gases on the Green River shale, and perhaps other materials, can be attributed to the difference in their saturated vapor pressures. The slight deviation of curves between different gases from a single trend probably is related to the properties of the oil shale sample. These include its porosity or pore sizes relative to the molecular size of the gases, and the absorption capacity of different gases in the organic matter in the shale.

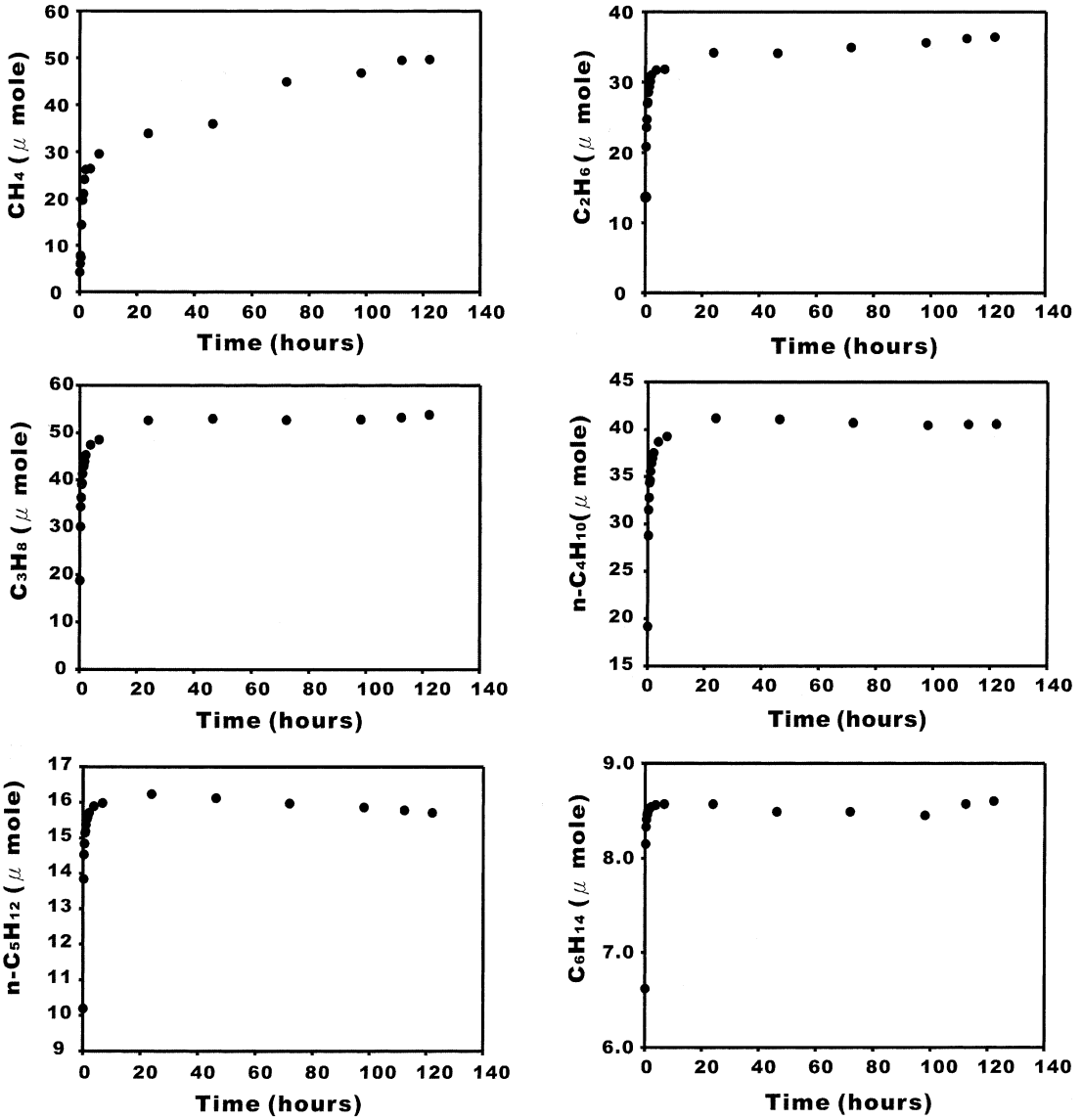

Fig. 10. The amounts of hydrocarbon gases adsorbed on 10 g of Green River shale as a function of time. The solid circles are experimental data at 26 °C and 1.1 atm.

3.3. Adsorption rate

The adsorption rates to reach steady state (or near saturation) also vary with different combinations of adsorbents and adsorbates. The adsorption rates of C_2 gas relative to C_1 on activated carbon is significantly faster than for other adsorbents since it is completed within two hours. The adsorption of C_2 relative to C_1 on other materials was completed in a much longer time, up to 80 h (Fig. 8). The same is also true for the change of adsorptive amounts as a function of time. It has been shown that in most cases the rate is rapid in the first 2–20 h, and then it slows and approaches a steady state in about 50–150 h. For example, in the case of shaly coal, the adsorption was completed within 10 h for C_6, 60 h for C_5, 150 h for C_2, C_3, and C_4, and 250 h or more for C_1 (Fig. 9). In the case of Green River shale, the adsorption was completed within 20 h for C_3–C_6 and 120 h for C_2, whereas it was close to completion up to 120 h for C_1 (Fig. 10). The data also show that the time periods required for completing the adsorption of each adsorbate on most of the studied adsorbents generally decrease with increasing carbon number of hydrocarbon gases. In general, the relatively fast adsorption of hydrocarbon gases (C_1–C_6) on the studied geological materials imply that adsorption kinetics is not a factor

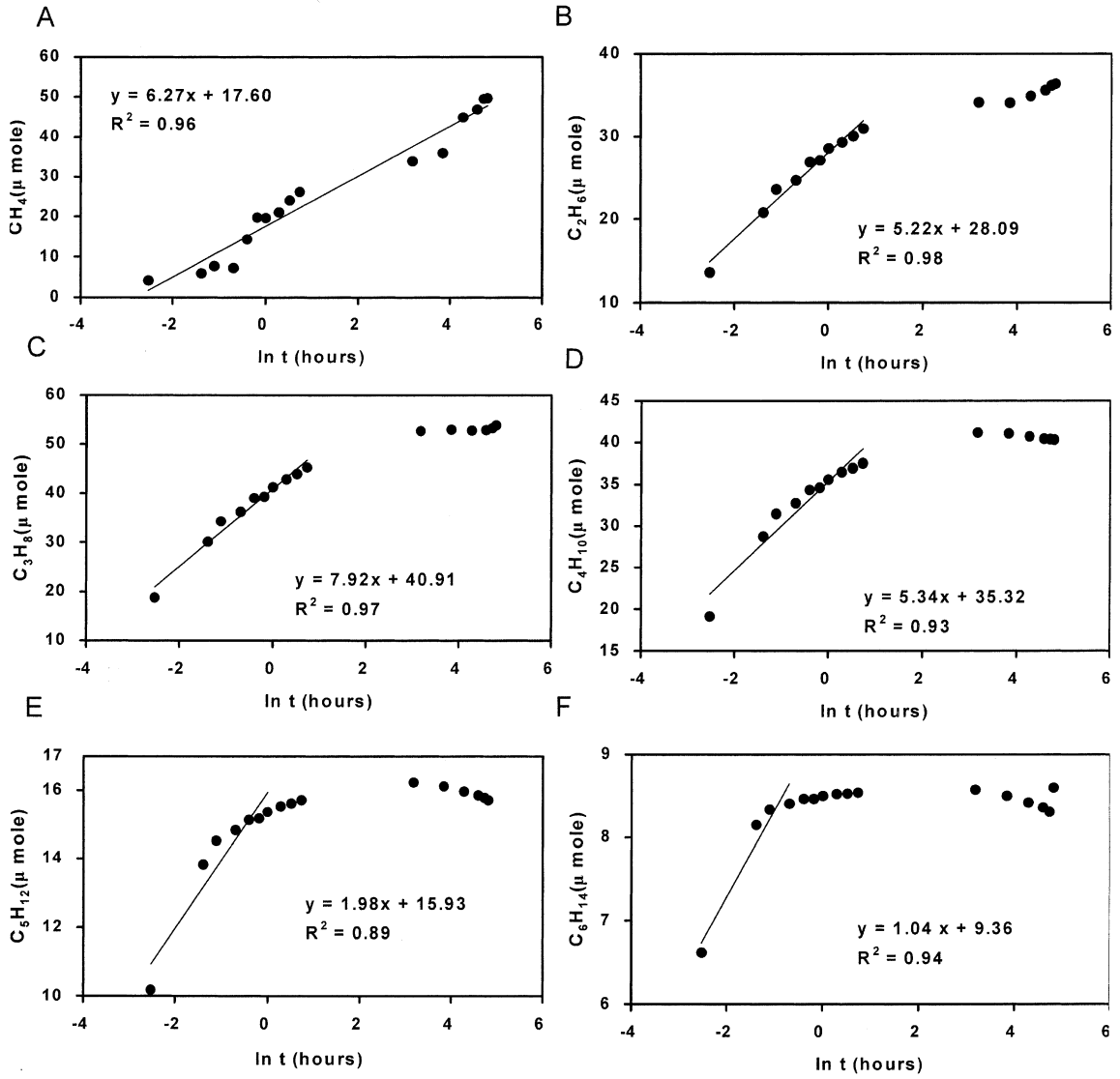

Fig. 11. The amounts of hydrocarbon gases adsorbed on 10 g of Green River shale as a function of time in logarithm scale. The solid circles are experimental data while solid lines are results modeled by fitting parts of the data to the Elovich kinetic equation. The data points near equilibrium are excluded from the kinetic fitting.

in affecting compositional fractionation during the migration of hydrocarbon gases.

The Elovich model which is commonly used for sorption kinetic analysis (Cheung et al., 2001) has been applied to model our experimental results. The Elovich kinetic equation can be expressed by:

$$dq/dt = a \exp(-bq) \quad (1)$$

The integration of (1) gives:

$$q = (1/b) \ln(1 + abt) \quad (2)$$

or

$$q = (1/b) \ln(ab) + (1/b) \ln(t + t_o) \quad (3)$$

where q is adsorptive amount, t is time, $t_o = (1/ab)$, a and b are parameters of the equation. The parameter a represents the initial adsorption rate when q equals zero, whereas b is related to the extent of surface coverage and activation energy for chemisorption (Low, 1960). If $abt \gg 1$, Eq. (3) (Harvlin et al., 1985; Stucki and Lee, 1999) can be simplified to:

$$q = (1/b) \ln(ab) + (1/b) \ln(t) \quad (4)$$

Our data for oil shale were fitted to the kinetic model by plotting q as a function of $\ln(t)$, and a and b can be calculated from the slope and intercept of the linear Eq. (4). It is shown that the experimental data for methane are consistent with linear relationships of Eq. (4) predicted by the model (Fig. 11). In this case, the calculated a and b values are, respectively, 85.6 and 0.16 for methane. For C_2–C_6 hydrocarbon gases, the deviation of data from the model at longer time indicates the approach of equilibrium (Fig. 11). Excluding the data points near equilibrium, the calculated a and b values are, respectively, 1153 and 0.19 for ethane, whereas those for propane are 1308 and 0.13.

4. Conclusion

The influence of adsorption process on the compositional variations in hydrocarbon gases migrating through clays (kaolinite and montmorillonite), and organic matter (coal, oil shale and activated-carbon) has been experimentally studied. This study is one of a few experimental studies for determining adsorption capacities and selectivity of a hydrocarbon gas mixture on geological materials. The results reveal a strong preferential adsorption of wet hydrocarbon gases over methane. The adsorption selectivity among the C_2–C_6 hydrocarbon gases has also been quantified and shows that there is stronger adsorption for the heavier gas molecules, confirming that the selectivity results mainly from the variations in their vapor pressures. The adsorption of hydrocarbon gases on coal and organic rich-shale is stronger than clays. The adsorption of methane and wet gases on clays, although less than that for organic matter, is significant. This study also provides new information on the adsorption rates of the hydrocarbon gases on geological materials. Although the applications of this study to the migration of hydrocarbon gases in the subsurface are limited, the present study provides basic information for future experiments, which may mimic more closely the migration paths in hydrocarbon systems.

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