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Adsorption Properties of Hydrocarbons (n-Decane, Methyl Cyclohexane and Toluene) on Clay Minerals: An Experimental Study

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Abstract: Adsorption of hydrocarbons may significantly affect hydrocarbon migration in unconventional reservoirs. Clay minerals form the primary adsorbent surfaces for hydrocarbons adsorbed in mudstone/shale. To study the adsorption properties of hydrocarbons (n-decane (C10H22), methyl cyclohexane (C7H14) and toluene (C7H8)) on clay minerals (i.e., cookeite, ripidolite, kaolinite, illite, illite/smectite mixed-layer, Na-montmorillonite and Ca-montmorillonite), hydrocarbon vapor adsorption (HVA) tests were conducted at 298.15 K. The results showed that (i) the adsorption amounts of C10H22, C7H14 and C7H8 ranged from 0.45–1.03 mg/m², 0.28–0.90 mg/m² and $0.16-0.53 \text{ mg/m}^2$, respectively; (ii) for cookeite, ripidolite and kaolinite, the adsorption capacity of C10H22 was less than C7H14, which was less than C7H8; (iii) for illite, Na-montmorillonite and Ca-montmorillonite, the adsorption capacity of C10H22 was greater than that of C7H8, and the adsorption capacity of C7H14 was the lowest; (iv) for an illite/smectite mixed-layer, C7H14 had the highest adsorption capacity, followed by C10H22, and C7H8 had the lowest capacity. Adsorption properties were correlated with the microscopic parameters of pores in clay minerals and with experimental pressure. Finally, the weighted average method was applied to evaluate the adsorption properties of C10H22, C7H14 and C7H8 on clay minerals in oil-bearing shale from the Shahejie Formation of Dongying Sag in the Bohai Bay Basin, China. For these samples, the adsorbed amounts of C7H14 ranged from 18.03–28.02 mg/g (mean 23.33 mg/g), which is larger than that of $C_{10}H_{22}$, which ranges from 15.40–21.72 mg/g (mean 18.82 mg/g). The adsorption capacity of C7H8 was slightly low, ranging from 10.51–14.60 mg/g (mean 12.78 mg/g).

Keywords: hydrocarbon vapor adsorption (HVA); adsorption property; n-decane; methyl cyclohexane; toluene; clay minerals

1. Introduction

The adsorption of hydrocarbons may affect hydrocarbon migration in the subsurface [1], which significantly impacts the recovery from unconventional reservoirs [2–6]. Clay minerals form the primary adsorbent surface for adsorbed hydrocarbons in mudstone/shale [7–10]. In recent decades, the adsorption behavior of CH₄ on clay minerals has been studied extensively in a large number of laboratory experiments [11–14]. In addition to CH₄, a few studies were conducted using C₂H₂ [11,12],

and a gas mixture of C₁–C₆ alkanes [15]. It is generally considered that CH₄ adsorption capacity of clay minerals is determined by its pore volume and specific surface area [16,17]. However, due to the dramatic differences in physicochemical properties between liquid and gas, previously proposed techniques [14,18–25] and models (including Freundlich [26,27], Langmuir [28], and Dubinin-Astakhov [29–31]) for gas adsorption are not appropriate to evaluate hydrocarbon in a liquid state.

Usually, hydrocarbon-solution adsorption tests were used to determine adsorption capacity of liquid hydrocarbon on porous media [32–45]. First, mixed hydrocarbons (e.g., crude oil, asphaltene, maltene and resin) are diluted using an organic solvent (e.g., toluene and n-heptane) to a certain concentration. Then, experiments are carried out to determine the adsorption capacity of minerals (e.g., clay minerals, quartz, feldspar, calcite and dolomite) as a function of equilibrium time or hydrocarbon concentration under a certain temperature. Previous studies showed the following: (1) for shale-oil, clay minerals had the highest adsorption capacity (18.0 mg/g), quartz had an intermediate value (3.0 mg/g), and carbonates had the lowest adsorption capacity (1.8 mg/g) [39]; (2) for quartz, the adsorbed amount (2 mg/g) of asphaltene [36], which was diluted with a solution of n-heptane and toluene, is apparently lower than that of asphaltene diluted with toluene (4.5 mg/g) [45] and 6.4 mg/g [44]; (3) feldspar has a greater adsorption capacity than quartz [45]; (4) for calcite, the maximum adsorbed amount of polar compounds (resin and asphaltene) is 2.1–3.6 mg/g [42]; and (5) when compared to limestone, dolomite has a smaller adsorption capacity and a smaller adsorbed amount of asphaltene [46].

Examination of the adsorption behavior of a hydrocarbon solution should consider the interactions of the adsorbent, solute (i.e., adsorbate) and solvent. Usually, greater interaction between the adsorbent and solute results in a larger adsorption capacity. Nevertheless, interaction between the solute and solvent can prevent the adsorbent adsorbing the solute from the solvent, negatively affecting the adsorption process. These complexities require a new method to study adsorption properties of liquid hydrocarbons on clay minerals.

In order to account for the complex constituent clay minerals in oil-bearing mudstone/shale, we use hydrocarbon vapor adsorption (HVA) tests to evaluate the adsorption properties of hydrocarbons (n-decane (C₁₀H₂₂), methyl cyclohexane (C₇H₁₄) and toluene (C₇H₈)) on different clay minerals (i.e., cookeite, ripidolite, kaolinite, illite, illite/smectite mixed-layer, Na-montmorillonite and Ca-montmorillonite) by obtaining adsorption isotherms with increasing relative pressure at 298.15 K [47,48]. Furthermore, we investigate the impact of microscopic parameters (specific surface area, pore size distribution, pore volume, etc.) related to pores in clay minerals and pressure on the adsorption properties of C₁₀H₂₂, C₇H₁₄ and C₇H₈ on clay minerals. Finally, we evaluate the adsorption properties of C₁₀H₂₂, C₇H₁₄ and C₇H₈ on clay minerals in oil-bearing shale from the Shahejie Formation of the Dongying Sag in the Bohai Bay Basin, northern China.

2. Materials and Methods

2.1. Materials

The pure clay minerals of cookeite (CAr-1), ripidolite (CCa-2), kaolinite (KGa-1b), illite (IMt-2), illite/smectite mixed-layer (ISCz-1), Na-montmorillonite (SWy-2) and Ca-montmorillonite (STx-1b) were obtained from the Clay Minerals Society. Baseline Studies (e.g., composition, geologic origin, infrared (IR) analysis, thermal analysis, chemical analysis and cation exchange capacity) of clay minerals from the Clay Minerals Society are available [49–58].

Oil-bearing shale samples (B172, F169, F41, H172, H88, L76, LX884 and Y556) were obtained from the primary shale formations of different petroleum well boreholes in the Dongying sag of the Bohai Bay basin, China. In the sag, the development of lacustrine mudstone/shale formations was widespread in the Eocene Shahejie Formation, mainly including the Middle and Lower-third Member (Es³² and Es^{3×}) and the Upper-fourth Member (Es^{4*}). As one of the prospective districts in China for shale oil development, abundant oil-gas resources have been discovered recently in the shale formations from the Es^{3×} and Es^{4*} sub-members of the sag [48].

All clay samples were milled into powder particles at 40–60 mesh (250–425 μ m) by an agate mortar. Then, each sample was subdivided into three parts, which were tested for HVA, low-temperature nitrogen adsorption/desorption (LT-N₂A/D) and low-pressure carbon dioxide adsorption (LP-CO₂A). The objective of these tests was to obtain the adsorption isotherms of hydrocarbons and the microscopic parameters of pores in clay minerals.

2.2. HVA Test

HVA tests were conducted for the n-decane (C₁₀H₂₂), methyl cyclohexane (C₇H₁₄) and toluene (C₇H₈) adsorption on clay minerals using a 3H-2000PW Gravimetry Vapor Sorption Analyzer [48]. Prior to the test, the samples were heated at 383.15 K to remove residual gas and water in the sample [59–61]. The equipment and procedure used here is the same as that used in HVA tests of C₁₀H₂₂ at a certain relative pressure that are detailed in a previous study by Li et al. [48]. In this study, the experimental temperature is held constant at 298.15 K. Because it is difficult to precisely control the experimental pressure due to the large carbon numbers of the hydrocarbons, adsorption isotherms for C₁₀H₂₂, C₇H₁₄ and C₇H₈ were only measured at several non-uniform relative pressure points. The highest relative pressures (P/P_0) measured were 0.8 P/P_0 for C₁₀H₂₂ and 0.9 P/P_0 for C₇H₁₄ and C₇H₈. Under 0.8 P/P_0 and 298.15 K conditions, the total amount (Q_t) of C₁₀H₂₂ accumulating on clay minerals was measured. Under 0.9 P/P_0 and 298.15 K conditions, the total amounts (Q_t) of C₇H₁₄ and C₇H₁₄ and

2.3. LT-N2A/D and LP-CO2A Tests

LT-N₂A/D isotherms were measured over relative pressures ranging from approximately 10⁻⁵ to 0.995 using an Autosorb-iQ-Station-1 instrument at 77 K [48] to obtain the pore size distributions (PSD), pore volumes and specific surface areas of the clay minerals. The maximum pore diameter (d_{max}) (306.42–385.55 nm) was directly determined by Barrett-Joyner-Halenda (BJH) method [62]. The minimum pore diameter (d_{min}) (1.17–1.22 nm) was obtained by density functional theory (DFT) [63]. In addition, LP-CO₂A tests were carried out on an Autosorb-IQ-MP instrument at 273.15 K to obtain the pore size distribution of pores with the size of 0.305–1.475 nm. According to the classification of the International Union of Pure and Applied Chemistry (IUPAC), pores were subdivided into micropores (<2 nm in diameter), mesopores (2–50 nm in diameter) and macropores (>50 nm in diameter) [64]. LT-N₂A/D and LP-CO₂A tests referred to the People's Republic of China petroleum natural gas profession standard (SY/T 6154-1995) and National Standards of the People's Republic of China (GBT 21650.3-2011), respectively.

2.4. XRD

The constituent clay minerals of the oil-bearing shale samples (B172, F169, F41, H172, H88, L76, LX884 and Y556) were analyzed using a Bruker D8 DISCOVER X-ray diffraction at 295.15 K temperature and 35% humidity. The radiation source was Cu.

3. Results and Discussion

3.1. Adsorption Properties of C10H22, C7H14 and C7H8 on Clay Minerals

The amount of hydrocarbon measured during the tests contains two parts: adsorption and capillary condensation. As shown in Figure 1, from the $P/P_0 \approx 0$, the amount of hydrocarbons adsorbed by clay minerals made up most of the total amount of hydrocarbon measured during the tests and is closely related to the specific surface area of clay minerals. With increasing relative pressure ($0 < P/P_0 < 1$), capillary condensation begins to appear on the interspace of pores. At relatively high pressures, condensed rather than adsorbed hydrocarbon became the larger contributor to the total amount of hydrocarbon measured during the tests. Accordingly, at certain relative pressures (i.e., inflection points), the amount of hydrocarbon measured per unit surface area

(*n*_{BET}) accurately reflects the adsorption of hydrocarbons on clay minerals, and the values of *n*_{BET} are assumed to the adsorbed amount per unit surface area.



Figure 1. Schematic of the adsorption and condensation of hydrocarbon with increasing relative pressure.

As shown in Figure 2, correlation coefficients (R^2) between BET surface areas (A_{BET}) and tested amounts of hydrocarbon (Q) for $C_{10}H_{22}$, C_7H_{14} and C_7H_8 increase linearly at the early stages of pressure increase, but then deviate from the straight lines (even decreasing for $C_{10}H_{22}$ and C_7H_8). These inflection points occur at approximately 0.65 P/P₀ (C₁₀H₂₂), 0.4 P/P₀ (C₇H₁₄) and 0.3 P/P₀ (C₇H₈). Theoretically, high R^2 values reflect the dominance of the adsorption process of hydrocarbons on pore surfaces, and low R^2 values are mainly attributed to the apparent dominance of capillary condensation. As shown in Figure 2a–c, the correlation coefficient (R^2) for total pore volume (V_i) and tested amount of hydrocarbon (Q) continues to increase when P/P_0 is larger than the inflection point. If capillary condensation had no effect, then the R^2 values for V_t and Q would decrease with decreasing R^2 values for A_{BET} and Q because total pore volume is proportional to BET surface area (Figure 3a). In Figure 2b, as P/P_0 becomes larger than the P/P_0 at the inflection point, the value of the correlation coefficient (R^2) of A_{BET} and Q does not decrease but deviates from the straight line. For C_7H_{14} , the capillary condensation may not be strong enough to cause the decrease in R^2 value, since when compared with C10H22 and C7H8, C7H14 has the smallest radius of capillary condensation according to the classical Kelvin equation [65]. Therefore, at the inflection points, the amount of hydrocarbon per unit surface area measured during the test (i.e., *nBET*) (Table 1) can be used to evaluate the adsorption properties of hydrocarbons on clay minerals.



Figure 2. Correlation coefficients for BET surface area and tested hydrocarbon amount (R^2 of A_{BET} -Q) shown with blue line and Y-axis, and correlation coefficients for total pore volume and tested hydrocarbon amount (R^2 of V_1 -Q) shown with red line and Y-axis for C₁₀H₂₂ (**a**), C₇H₁₄ (**b**) and C₇H₈ (**c**) with increasing relative pressure.



Figure 3. (a) Relationship between BET surface areas (*ABET*) and total pore volumes (*V*_{*i*}) of clay minerals; (b) total pore volumes (*V*_{*i*}) and BET surface areas (*ABET*) of clay minerals from LT-N₂A/D tests (a–g: Ca-montmorillonite, kaolinite, illite/smectite mixed-layer, Na-montmorillonite, illite, cookeite and ripidolite).

Table 1. Tested amounts (q_a) of C₁₀H₂₂, C₇H₁₄ and C₇H₈ measured at inflection points and the q_a per unit of surface area (*n*_{BET}) for clay minerals.

Class Min anala	Codes	n BE	т (mg/m	2)	<i>qa</i> (mg/g)			
		C10H22	C7H14	C7H8	C10H22	C7H14	C7H8	
cookeite	CAr-1	1.02	0.28	0.16	3.32 ± 0.05	0.91 ± 0.01	0.53 ± 0.02	
ripidolite	CCa-2	0.45	0.36	0.31	2.24 ± 0.01	1.81 ± 0.01	1.52 ± 0.02	
kaolinite	KGa-1b	0.73	0.34	0.23	8.90 ± 0.23	4.21 ± 0.02	2.85 ± 0.13	
illite	IMt-2	0.46	0.36	0.40	9.03 ± 0.03	7.03 ± 0.01	7.92 ± 0.04	
illite/smectite mixed-layer	ISCz-1	0.69	0.90	0.46	22.11 ± 0.08	28.67 ± 0.02	14.81 ± 0.03	
Na-montmorillonite	SWy-2	0.53	0.29	0.41	13.58 ± 0.06	7.45 ± 0.01	10.43 ± 0.04	
Ca-montmorillonite	STx-1b	0.83	0.42	0.53	80.24 ± 0.19	40.82 ± 0.04	51.47 ± 0.19	

For C₁₀H₂₂, the values of *n*_{BET} range from 0.45–1.03 mg/m² (mean 0.67 mg/m²). Cookeite has the greatest adsorption of C₁₀H₂₂, followed by Ca-montmorillonite. For C₇H₁₄, the values of *n*_{BET} range from 0.28–0.90 mg/m², with an average of 0.42 mg/m². The interaction between C₇H₁₄ and the illite/smectite mixed-layer is the most prominent among all the clay minerals. When compared with C₁₀H₂₂ and C₇H₁₄, the adsorption of C₇H₈ on clay minerals is relatively weak, with a range of 0.16–0.53 mg/m² (mean 0.35 mg/m²). For C₇H₈, Ca-montmorillonite has the largest *n*_{BET} (0.53 mg/m²), illite/smectite mixed-layer has the second largest value (0.46 mg/m²), and cookeite has the lowest adsorption value (0.16 mg/m²). The hydrocarbon amounts (*q*_a) tested at inflection points are shown in Table 1. Apparently, the adsorption capacities of C₁₀H₂₂, C₇H₁₄ and C₇H₈ on clay minerals; (b) for illite, Na-montmorillonite and Ca-montmorillonite, the adsorption capacity of C₁₀H₂₂, C₇H₁₄ has the highest adsorption capacity, followed by C₁₀H₂₂, and the C₇H₈ has the lowest capacity.

When the phenomenon of capillary condensation is considered [66], the amount of hydrocarbon measured at a certain P/P_0 includes both the adsorbed and condensed (i.e., free-phase-like liquid) hydrocarbon. Thus, the hydrocarbons measured at each experimental point represent the accumulated amount in clay minerals, which includes adsorbed and free hydrocarbons. As P/P_0 becomes extremely high, up to ~1, pore spaces will become completely filled with hydrocarbon in adsorbed and condensed states [48]. In this paper, the tested amounts (Q) of $C_{10}H_{22}$, C_7H_{14} and C_7H_8 with increasing P/P_0 are expressed in Figure 4; the accumulated amount of hydrocarbons in clay minerals increases with increasing P/P_0 . The accumulated amounts of C₁₀H₂₂ in clay minerals are presented in Figure 4a. At $P/P_0 = 0.8$, (a) the accumulated amount of hydrocarbon in Ca-montmorillonite is the largest, over 100 mg/g; (b) the accumulated amounts in Na-montmorillonite, the illite/smectite mixed-layer and kaolinite progressively decrease, ranging from 33.89–25.46 mg/g; (c) illite has a relatively low accumulated amount (14.09 mg/g); (d) the accumulated amount for cookeite is slightly higher than that of ripidolite, but both are extremely low with an average value of 4.31 mg/g. In Figure 4b–c, the amounts of C7H14 and C7H8 accumulated in clay minerals are presented. At $P/P_0 = 0.9$, the accumulated amount of C₇H₁₄ and C₇H₈ in Ca-montmorillonite is more than 100 mg/g, much higher than the accumulation amounts in the other clay minerals. For C₇H₈, Na-montmorillonite has a greater storage capacity than the illite/smectite mixed-layer, whereas for C₇H₁₄, the result is the opposite. The mean accumulated amount of C₇H₁₄ and C₇H₈ in kaolin is 21.05 mg/g, which is larger than the value (15.87 mg/g) for illite. Ripidolite has an extremely weak storage capacity of C₇H₁₄ and C₇H₈, with an average of 3.69 mg/g, which is slightly greater than that of cookeite (2.98 mg/g).



Figure 4. Tested amounts (*Q*) of C₁₀H₂₂ (**a**), C₇H₁₄ (**b**) and C₇H₈ (**c**) with increasing *P*/*P*₀ for clay minerals (CAr-1: cookeite; CCa-2: ripidolite; KGa-1b: kaolinite; IMt-2: illite; ISCz-1: illite/smectite mixed-layer; SWy-2: Na-montmorillonite; STx-1b: Ca-montmorillonite).

Therefore, in terms of relative amounts of accumulated hydrocarbons for $C_{10}H_{22}$, C_7H_{14} and C_7H_8 : Ca-montmorillonite \gg illite/smectite mixed-layer and Na-montmorillonite > kaolinite > illite > cookeite and ripidolite, which is different from the CH₄ adsorption capacity: montmorillonite \gg illite/smectite mixed-layer > kaolinite > chlorite > illite, as reported by Ji et al. [13].

3.2. Factors Influencing Hydrocarbon Adsorption on Clay Minerals

Microscopically, adsorption/desorption of hydrocarbon molecules on the surface of clay minerals is influenced by the intermolecular force. In addition, if the clay minerals adsorb hydrocarbon molecules, adsorption sites on the surface must be present. Therefore, the adsorption properties of C₁₀H₂₂, C₇H₁₄ and C₇H₈ are associated with the microscopic parameters (specific surface area, pore size distribution, pore volume, etc.) of pores in clay minerals, as well as the experimental conditions (temperature and pressure, etc.).

3.2.1. Microscopic Parameters of Pores in Clay Minerals

The adsorption properties of C₁₀H₂₂, C₇H₁₄ and C₇H₈ are associated with the microscopic parameters (specific surface area, pore size distribution, pore volume, etc.) of pores in clay minerals. In this study, the total pore volumes were measured by LT-N₂A/D tests. The specific surface area was calculated from the adsorption branch of the N₂ isotherm by the standard Brunauer-Emmett-Teller (BET) equation with relative pressure ranging from 0.05 to 0.3 [67]. Because of an extraneous peak located at ~3.8 nm in the PSD curves obtained using the BJH method [68], the PSDs (>1.475 nm in diameter) were determined by combining the DFT with BJH method using LT-N₂A/D tests, and other PSDs (<1.475 nm in diameter) were obtained by LP-CO₂A tests.

As shown in Figure 3b and Table 2, the BET surface areas (A_{BET}) range from 3.242–96.563 m²/g (mean 27.731 m²/g). Ca-montmorillonite has the largest specific surface area followed by the illite/smectite mixed-layer (31.959 m²/g) and Na-montmorillonite (25.421 m²/g). The BET surface areas for Ca- and Na- montmorillonite measured in this study are credible based on comparison with the BET surface areas (24.7–97 m²/g) of montmorillonite previously measured [11,69–73]. For illite and kaolinite, the BET surface areas (19.738 m²/g and 12.271 m²/g, respectively) decrease progressively but are larger than that of illite (17.5 m²/g) [74] and kaolinite (13.0 m²/g) [44]. Ripidolite (4.922 m²/g) has a slightly higher specific surface area than cookeite (3.242 m²/g) and is similar to chlorite with an A_{BET} of 4.8 m²/g as measured by Ross and Bustin [72]. Meanwhile, total pore volumes range from 8.9 × 10⁻³–278.2 × 10⁻³ cm³/g (mean 86.8 × 10⁻³ cm³/g). Ca-montmorillonite has the largest pore volume followed by kaolinite (136.38 × 10⁻³ cm³/g). The total pore volume (73.75 × 10⁻³ cm³/g) of the illite/smectite mixed-layer is approximately the same as that of Na-montmorillonite (71.96 × 10⁻³ cm³/g) and is significantly larger than that of illite (27.53 × 10⁻³ cm³/g). Cookeite and ripidolite both

have the lowest V_t (11.08 × 10⁻³ and 8.95 × 10⁻³ cm³/g, respectively). Thus, in the terms of relative specific surface areas and total pore volumes for clay minerals: Ca-montmorillonite > illite/smectite mixed-layer > Na-montmorillonite > illite > cookeite and ripidolite.

Table 2. BET surface areas (A_{BET}), total pore volumes (V_t) and the percentages of pore volumes from micropore, mesopore and macropore.



Figure 5. Pore size distribution for clay minerals from LT-N₂A/D and LP-CO₂A tests (**a**–**g**: cookeite, ripidolite, kaolinite, illite, illite/smectite mixed-layer, Na-montmorillonite and Ca-montmorillonite; green short dash line: Pore diameter = 0.82 nm; red short dash line: Pore diameter = 1.17 nm).

There is a part of pore volume (V_0) that is inactive and scarcely contributes to hydrocarbon adsorption because the pore diameters are less than the size of hydrocarbon molecules (d_0). When considering the complete entrance of molecule into the pore, d_0 should be determined by the maximal length of *n*-alkane molecule rather than the cross-sectional diameter. The maximal length of *n*-butane (C₄H₁₀) molecule is 0.8 nm and that of *n*-hexane (C₆H₁₄) is 1.1 nm [75]. The three-dimensional size of a toluene (C₇H₈) molecule is $0.380 \times 0.666 \times 0.818$ nm in its minimum energy configuration determined using Material Studio from Accelrys Inc., San Diego, CA, USA. Methyl cyclohexane (C7H14) and toluene (C7H8) are both composed of a six-membered carbocyclic ring (cyclohexane or benzene) and a methyl group (-CH₃). The cross-sectional area of cyclohexane is similar to that of benzene [76], thus the maximal length of C_7H_{14} is approximately equal to that of C7H8. Consequently, the molecule sizes of C10H22, C7H14 and C7H8 are larger than 1.1 nm, 0.818 nm and 0.818 nm, respectively. The volume of micropores (0.82–1.17 nm in diameter) (Figure 5) for clay minerals determined by the LP-CO₂A test only accounts for an average of 3.16% of the total pore volume measured using LT-N₂A/D tests. For the reasons given above, the pore volume of micropores can be simply measured by LT-N₂A/D tests. Deviations due to the exclusion of pores with sizes between d_0 and d_{\min} are insignificant and are considered negligible in this paper.

As mentioned previously, the adsorption capacities of C₁₀H₂₂, C₇H₁₄ and C₇H₈ are closely associated with the specific surface areas of the clay minerals, with correlation coefficients (R^2) of 0.985, 0.840 and 0.996, respectively (Figure 2). The relationship between the adsorbed amounts (q_a) of C₁₀H₂₂, C₇H₁₄ and C₇H₈ and the pore volume for micropores, mesopores and macropores measured using LT-N₂A/D tests are shown in Figure 6. The adsorbed amounts (q_a) are proportional to the pore

volumes of mesopores rather than that of micropores or macropores. The percentages of active micropores in clay minerals are too small, considering the diameter of *n*-decane, methyl cyclohexane and toluene molecules; in macropores, hydrocarbons are main capillary condensed rather than adsorbed; most clay minerals are dominated by mesopores, thus the adsorbed hydrocarbons mainly exist in mesopores.



Figure 6. Relationships between the adsorbed amounts (q_a) and the pore volume of micropores (**a**), mesopores (**b**) and macropores (**c**).

3.2.2. Pressure

The adsorption properties of C₁₀H₂₂, C₇H₁₄ and C₇H₈ on clay minerals are closely associated with the experimental conditions (temperature and pressure, etc.) during HVA tests. In this study, the experimental temperature was held constant at 298.15 K, and the relative pressure (*P*/*P*₀) varied between 0 and 1. As shown in Figure 7, for one clay mineral sample (i.e., same microscopic parameters of pores), the features of three curves of C₁₀H₂₂, C₇H₁₄ and C₇H₈ are different. When considering series of samples with the same radius of capillary condensation (i.e., synchronous processes of capillary condensation), the differences and relative changes in the amount of hydrocarbon tested are mainly controlled by the change of adsorption properties with increasing relative pressures.



Figure 7. Relationship between radius of capillary condensation (r_k) and the tested amounts (Q) of C₁₀H₂₂, C₇H₁₄ and C₇H₈ (**a**–**g**: cookeite, ripidolite, kaolinite, illite, illite/smectite mixed-layer, Na-montmorillonite and Ca-montmorillonite).

The radius of capillary condensation (r_k) as a function of relative pressure (P/P_0) was obtained from the classical Kelvin equation [65]:

$$Ln P/P_{0} = -\frac{2\sigma V_{L}}{r_{k}RT}\cos\theta$$
⁽¹⁾

where σ and V_L are the surface tension and molar volume of the liquid, measured in dyne/cm and m³/mol, respectively; *R* is the gas constant, 8.314 m³·Pa/ (K·mol); *T* is the absolute temperature, K; and θ is the contact angle, which is commonly taken to be zero since the liquid hydrocarbon is assumed to completely wet the adsorbed film. As shown in Figure 7, the tested amounts of C₁₀H₂₂,

C₇H₁₄ and C₇H₈ on clay minerals are considered as a function of Kelvin radius, which was fitted to Equation (2) using a least square method in IBM SPSS Statistics software

$$Q = aLn(r_k) + b \tag{2}$$

where *Q* is the tested amount of hydrocarbon at the Kelvin radius *rk*. A series of fitting parameters (*a*, *b*) for C₁₀H₂₂, C₇H₁₄ and C₇H₈ are shown in Table 3. The parameter *a* can effectively represent the differences and relative changes of adsorption properties with increasing *rk* (or *P*/*P*₀). Comparing the value of *a*, clay minerals can be subdivided into Groups A, B and C. Cookeite, ripidolite and kaolinite are in Group A where the parameter *a* varies as follows: C₁₀H₂₂ > C₇H₁₄ > C₇H₈. Illite, the illite/smectite mixed-layer and Ca-montmorillonite are in Group B where the parameter *a* is C₁₀H₂₂ > C₇H₁₄. Na-montmorillonite is in Group C where the parameter *a* is C₇H₈ > C₁₀H₂₂ > C₇H₁₄.

Class Minorals	Cadaa	C1	0 H 22	C7H14		C7H8	
Clay Minerals	Codes	а	b	а	b	а	b
cookeite	CAr-1	2.013	-1.172	1.113	-0.068	0.695	0.074
ripidolite	CCa-2	1.405	-0.614	0.965	0.882	0.883	0.852
kaolinite	KGa-1b	12.469	-15.198	7.181	-1.718	4.965	-0.332
illite	IMt-2	4.772	-0.693	3.450	3.588	3.760	4.956
illite/smectite mixed-layer	ISCz-1	11.650	-4.376	9.531	17.084	10.010	6.903
Na-montmorillonite	SWy-2	12.044	-8.134	7.687	0.481	12.207	1.125
Ca-montmorillonite	STx-1b	44.401	-10.915	32.072	7.696	33.032	25.228

Table 3. Fitting parameters *a* and *b* for C₁₀H₂₂, C₇H₁₄ and C₇H₈.

3.3. Application in Oil-Bearing Shale

The tested amounts (q_a) of C₁₀H₂₂, C₇H₁₄ and C₇H₈ measured at inflection points for clay minerals have been analyzed above (Table 1); these are assumed to be the adsorbed hydrocarbons. According the weighted average method, the total adsorbed hydrocarbon (Q_a) per gram of clay minerals in shale is simply equal to the sum of that (q_a) of every clay mineral based on the percentage of clay mineral constituents, expressed as

$$Q_a = \sum_{i=1}^n x_i q_{ai} \tag{3}$$

where x_i and q_{ai} are the *i*-th clay mineral fraction in shale and its adsorbed hydrocarbon, measured as a percentage and in mg/g, respectively. The q_a of chlorite is equal to the mean value of q_a of cookeite and ripidolite. The constraint condition is

$$\sum_{i=1}^{n} x_i = 1$$
 (4)

The clay mineral constituents of shale samples from the Shahejie Formation of the Dongying Sag in the Bohai Bay Basin, China, are mainly illite/smectite mixed-layer (Table 4). Recently, the equilibrium sorption amount for clay minerals was assigned as 18.0 mg/g on the assessment model of adsorbed and free shale-oil [39,77], which is based on 12 groups of hydrocarbon-solution tests of clay minerals separated from different mudstones/shales in the Shahejie Formation. In this study, the adsorbed amounts (Q_a) of C₁₀H₂₂ on clay minerals ranged from 15.40–21.72 mg/g (mean 18.82 mg/g) (Table 4). This range is smaller than that of C₇H₁₄, with a range of 18.03–28.02 mg/g (mean 23.33 mg/g). Compared to C₁₀H₂₂ and C₇H₁₄, the adsorbed capacity of C₇H₈ is the smallest, with a range of 10.51–14.60 mg/g (mean 12.78 mg/g).

Well	Stage	Depth (m)	Clay	Miner	al Con	Q_a (mg/g)				
			K	С	Ι	S	I/S	C10H22	C7H14	C7H8
B172	$Es_{3^{x}}$	3127.30	0	8	20	/	72	17.95	22.16	12.33
F169	$\mathrm{Es}_{4^{\mathrm{s}}}$	3697.00	6	13	26	/	55	15.40	18.03	10.51
F41	$Es_{3^{x}}$	2918.66	5	3	14	/	78	19.04	23.60	12.83
H172	$Es_{3^{x}}$	3336.80	4	2	19	/	75	18.71	23.03	12.75
H88	$Es_{3^{x}}$	3042.60	6	2	19	/	73	18.45	22.54	12.51
L76	Es_{4^s}	3780.42	0	0	3	/	97	21.72	28.02	14.60
LX884	Es_{4^s}	3506.20	0	0	3	/	97	21.72	28.02	14.60
Y556	Es ₃ x	2448.31	4	3	26	/	67	17 60	21 25	12 13

Table 4. Clay mineral constituents and total adsorbed hydrocarbon per gram of clay minerals in shale samples.

 $Es_{3^{x}}$: lower-third Member in the Eocene Shahejie Formationl; $Es_{4^{s}}$: upper-fourth Member in the Eocene Shahejie Formation; Q_{a} : total adsorbed hydrocarbon per gram of clay minerals; K: kaolinite; C: chlorite; I: illite; S: smectite; I/S: illite/smectite mixed-layer.

4. Conclusions

This study used HVA tests for evaluating the adsorption properties of *n*-decane (C₁₀H₂₂), methyl cyclohexane (C₇H₁₄) and toluene (C₇H₈) on different clay minerals (i.e., cookeite, ripidolite, kaolinite, illite, illite/smectite mixed-layer, Na-montmorillonite and Ca-montmorillonite) at 298.15 K. The results showed the following:

- (1) The tested amounts per unit surface area (*n*_{BET}) measured at inflection points accurately reflects the interaction between clay minerals and hydrocarbons. As a whole, the *n*_{BET} for C₁₀H₂₂ ranged from 0.45–1.03 mg/m² (mean 0.67 mg/m²), and the *n*_{BET} for C₇H₁₄ ranged from 0.28–0.90 mg/m² (mean 0.42 mg/m²).
- (2) The adsorption properties of C₁₀H₂₂, C₇H₁₄ and C₇H₈ are associated with the specific surface areas, the pore volumes of mesopores and experimental pressures. In terms of relative specific surface areas and total pore volumes in clay minerals: Ca-montmorillonite > illite/smectite mixed-layer > Na-montmorillonite > illite > cookeite and ripidolite. Kaolinite has a larger pore volume than the illite/smectite mixed-layer, but a smaller specific surface area than illite.
- (3) In the Shahejie Formation, Dongying Sag, Bohai Bay Basin, China, the adsorbed amounts of C₇H₁₄ on clay minerals from shale samples ranges from 18.03–28.02 mg/g (mean 23.33 mg/g), which is larger than that of C₁₀H₂₂, which ranges from 15.40–21.72 mg/g (mean 18.82 mg/g). The adsorbed capacity of C₇H₈ was the smallest, with a range of 10.51–14.60 mg/g (mean 12.78 mg/g). The values are similar to the adsorption properties of the main clay mineral (i.e., illite/smectite mixed-layer) in the shale samples.

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