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Experimental Determination of P-V-T-X Properties and Sorption Kinetics in the CO_2-CH_4-H_2O System under Shale Gas Reservoir Conditions: Part One, P-V-T-X Properties, Sorption Capacities and Kinetics of Model Materials for CO_2-CH_4 Mixtures to 125°C

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Introduction

Shale gas production via hydrofracturing has profoundly changed the energy portfolio in the USA and other parts of the world. Under shale gas reservoir conditions, CO_2 and H_2O, either in residence or injected during hydrofracturing or both, co-exist with CH_4. One important feature characteristic of shale is the presence of nanometer-scale (1-100 nm) pores in shale or mudstone. The interactions among CH_4, CO_2 and H_2O in those nano-sized pores directly impact shale gas storage and gas release from the shale matrix. Therefore, a fundamental understanding of interactions among CH_4, CO_2 and H_2O in nanopore confinement would provide guidance in addressing a number of issues encountered during the recovery process, such as rapid decline in production after a few years and low recovery rates. We are systematically investigating the P-V-T-X properties and adsorption kinetics in the CH_4-CO_2-H_2O system under reservior conditions.

We have designed and constructed a unique high temperature and pressure experimental system that can measure both P-V-T-X properties and adsorption kinetics sequentially. We are measuring the P-V-T-X properties of CH_4-CO_2 mixtures with CH_4 up to 95 vol. %, and adsorption kinetics of various materials, under conditions relevant to shale gas reservoirs. We used three types of materials: (I) model materials, (II) single solid phases separated from shale samples, and (III) crushed shale samples from known shale gas producing formations and from shale gas barren formations. The model materials are well characterized in terms of pore sizes. Therefore, the results associated with the model material serve as benchmarks for our model development.

The P-V-T-X properties obtained in this study will be used ro establish a high precision equation of state (EOS) applicable to shale gas recovery in confined nano-pore environments. An equation of state (EOS) that can accurately describe interactions in the CH_4–CO_2–H_2O system for a wide range of ionic strengths in a confined environment is an important and essential tool that enables efficient resource recovery from fewer, and less environmentally impactful wells. However, such an EOS does not exist at present. For the bulk properties, Duan et al. (1992) proposed an EOS for the CH_4–CO_2–H_2O system. Their EOS was based almost solely on experimental data for the following binary systems, i.e., CH_4–H_2O, CO_2–H_2O, and CH_4–CO_2. As they pointed out, "ternary data are almost nonexistent." In their parameterization, there were two experimental investigations addressing the ternary system as described in the following. Price (1981) measured solubility of CH_4 and CO_2 in brine containing 5 wt% NaCl at 150°C and 345 bars. Ramboz et al. (1985) investigated the CH_4–CO_2–H_2O system at temperatures above 370°C, which is not applicable to the conditions for shale gas recovery. After the publication of Duan et al. (1992), a number of studies on the CH_4–CO_2–H_2O system at temperatures below room temperature were initiated. The aim of these studies was to determine the hydrate equilibrium (e.g., Bruusgaard et al., 2010), but again these studies are not relevant to the conditions applicable for shale gas recovery. For the CO_2 + H_2O and CH_4 + H_2O binary systems, the most recent work is at 200°C and 250°C (Capobianco et al., 2013) and at 300°C, 400°C and 500°C (Lin, 2005), respectively, again, not applicable to shale gas recovery.

Sorption capacities, sorption and desorption kinetics are highly relevant to shale gas recovery. We systematically measure sorption capacities, sorption and desorption kinetics of the afore-mentioned three types of materials under reservoir relevant conditions. These results will be used for molecular dynamics (MD) modeling of the interactions in a multiple component system.

Experimental Methods

In this study, we employed the gravimetric method using a Netzsch STA 409 thermal gravimetric analyzer (TGA) with differential scanning calorimeter (DSC) and Differential temperature analyzer (DTA) that is adapted for measurement of adsorption capacities and kinetics of the three types of materials at reservoir relevant temperatures up to 125°C and constant pressures up to 1 bar. We studied the adsorption kinetics by monitoring the evolution of the weight change as a function of time from the instant a dose of CO_2 and CH_4 gas mixture is adsorbed onto the sample, until the moment saturation equilibrium is reached.

Results

In Figure 1, a typical sorption curve is presented. The linear portion of the curve is used for determination of sorption kinetics. The portion that indicates the sorption saturation has been attained is used for determination of sorption capacities. As an example, the sorption rates for activated carbon and montmorillonite are determined from the linear portion of the sorption curve as shown in Figures 2 through 4. We have used this methodology to measure the sorption capacities and kinetics for a series of model substances including activated carbon, crushed shale, illite and montmorillonite, up to 125°C.

In Table 1, the sorption capacities and sorption kinetics of activated carbon and montmorillonite (< 75 μm) for the mixture of 85% CH_4 and 15% CO_2 from 25°C to 125°C and the total pressure of 1 bar are summarized.

Table 1. Experimental measurements of sorption capacities and sorption rates for the model substances at 1 bar totol pressure

Model Substances	Temp, °C	Gas Mixture, volume percent	Pressure, bar	Sorption Capacity, mg/g	Sorption Rate, mg/g min^{-1}
DARCO activated carbon	25	85% CH_4 + 15% CO_2	1	28	0.68
	50	85% CH_4 + 15% CO_2	1	11	0.59
	75	85% CH_4 + 15% CO_2	1	9.0	0.31
	100	85% CH_4 + 15% CO_2	1	2.1	0.14
	125	85% CH_4 + 15% CO_2	1	1.8	0.10
Montmorillonite, <75 μm	25	85% CH_4 + 15% CO_2	1	2.8	4.7×10^{-2}
	50	85% CH_4 + 15% CO_2	1	0.30	9.6×10^{-3}
	75	85% CH_4 + 15% CO_2	1	0.19	6.7×10^{-3}
	100	85% CH_4 + 15% CO_2	1	0.18	5.1×10^{-3}
	125	85% CH_4 + 15% CO_2	1	0.12	3.3×10^{-3}

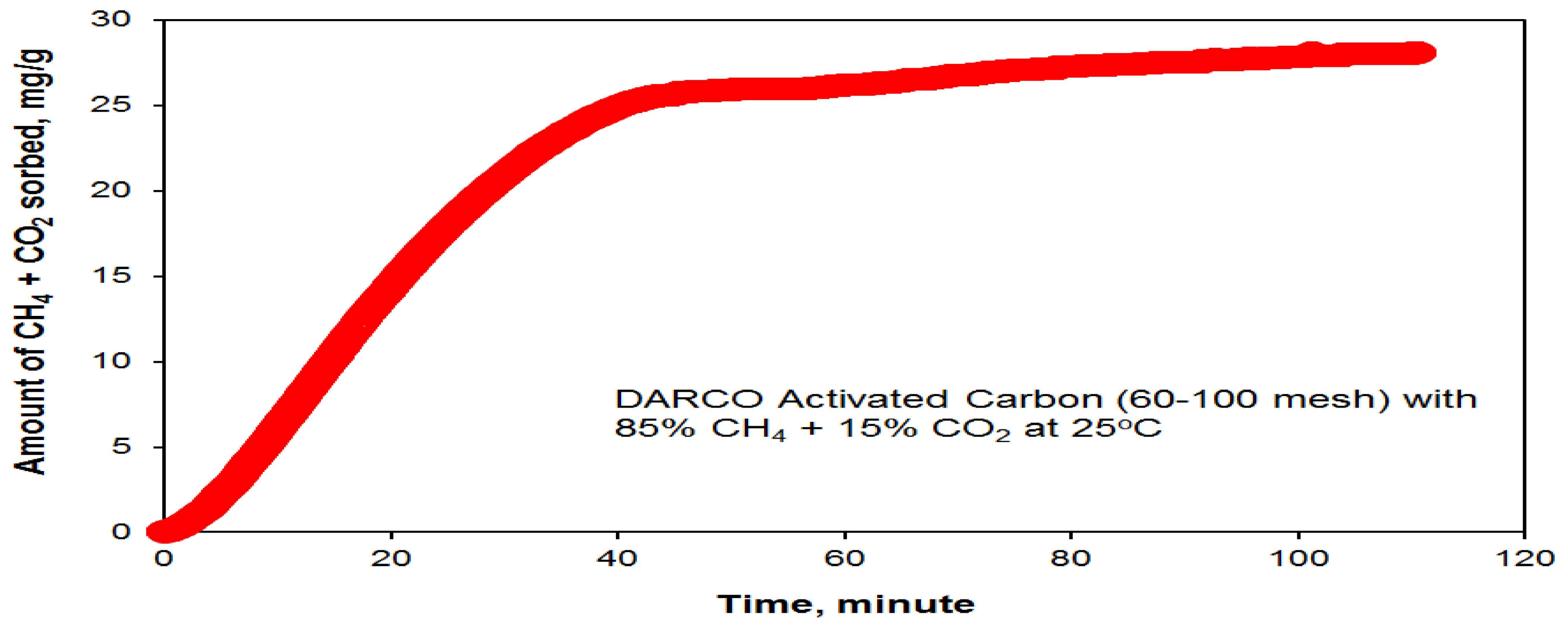

Figure 1. A plot showing sorption curve with CH_4 + CO_2 for activated carbon at 25°C and 1 bar.

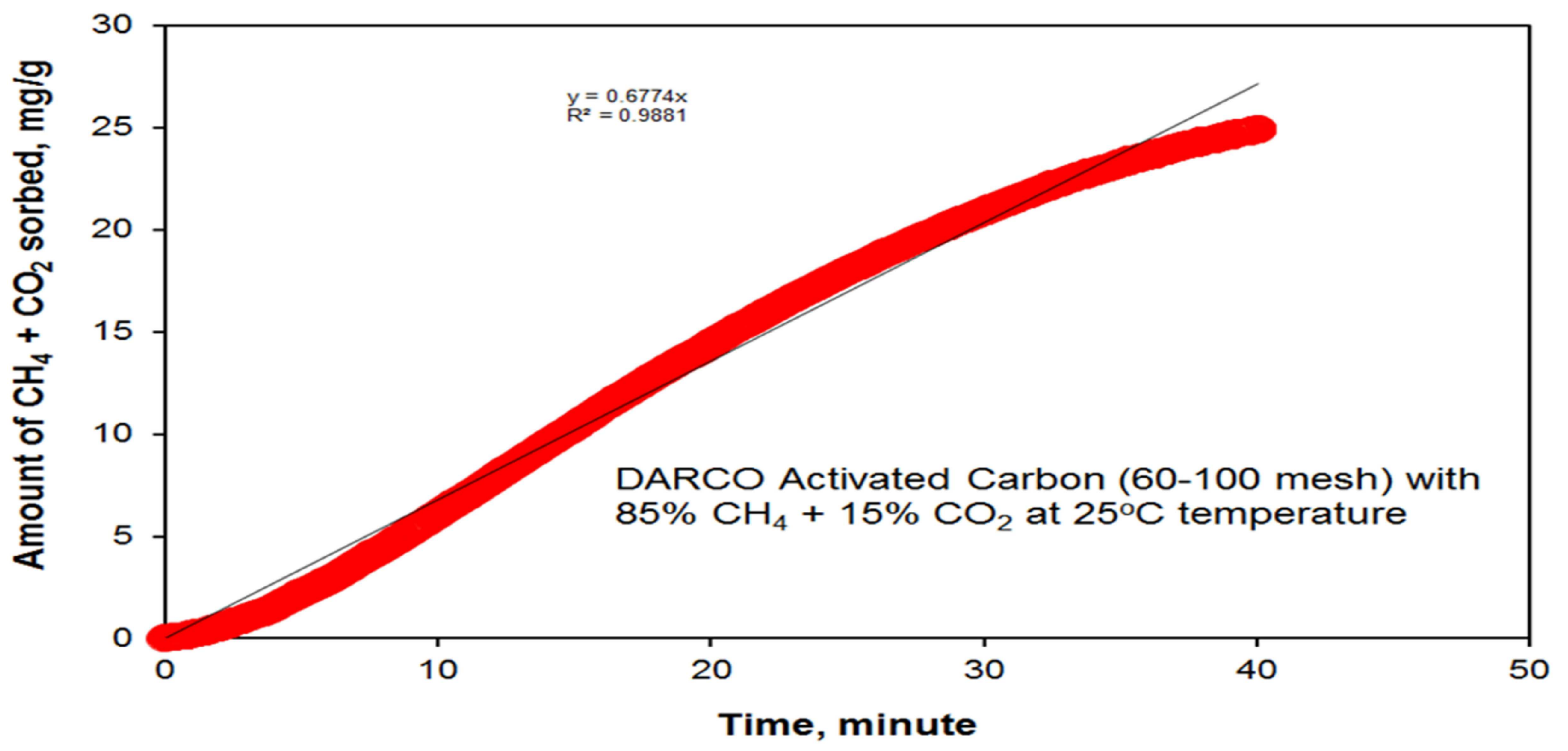

Figure 2. Sorption kinetics with CH_4 + CO_2 for activated carbon at 25°C and 1 bar.

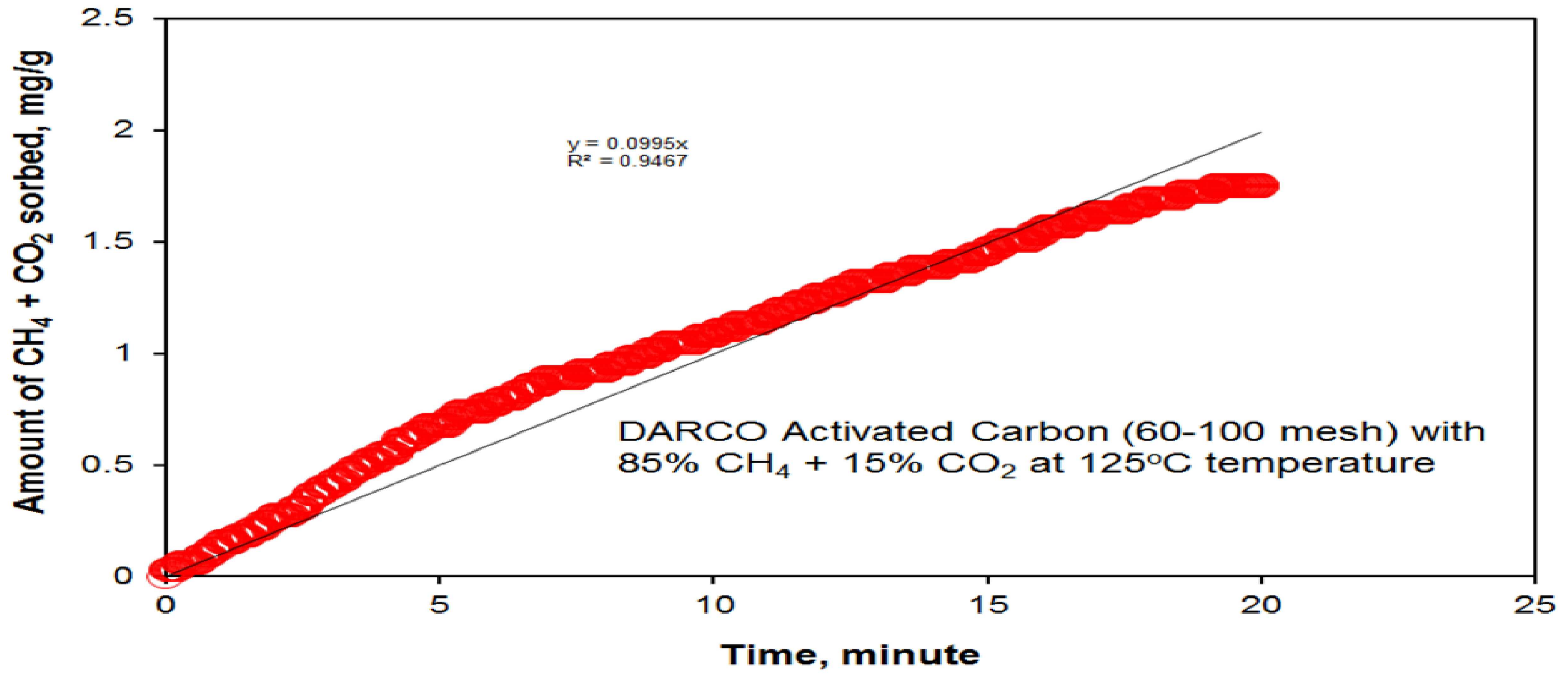

Figure 3. Sorption kinetics with CH_4 + CO_2 for activated carbon at 125°C and 1 bar.

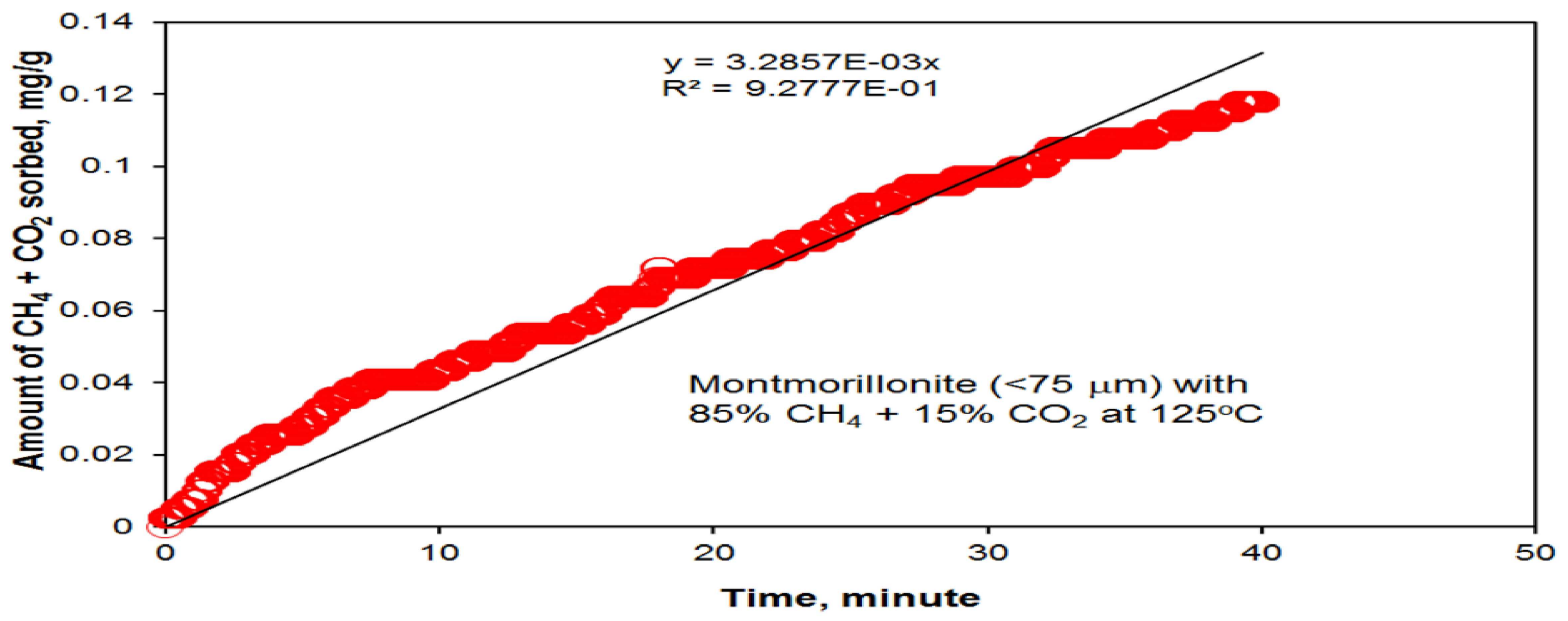

Figure 4. Sorption kinetics with CH_4 + CO_2 for montmorillonite at 125°C and 1 bar.

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References

Bruusgaard, H., Beltrán J.G., Servio, P., 2010. Solubility measurements for the CH_4 + CO_2 + H_2O system under hydrate–liquid–vapor equilibrium. Fluid Phase Equilibria 296, 106-109.

Duan, Z.-H., Moller, N., Weare, J.H., 1992. An equation of state for the CO_2—CH_4—H_2O system: II. Mixtures from 50 to 1000°C and 0 to 1000 bar. Geochimica et Cosmochimica Acta 56, 26 19-2631.

Krooss, B.M., van Bergen, F., Gensterblem, Y., Siemons, N., Pagnier, H.J.M., David, P. , 2002. High-pressure methane and carbon dioxide adsorption on dry and moisture-equilibrated Pennsylvanian coals. International Journal of Coal Geology, 51:69–92.

Lin, F., 2005, Experimental Study of the PVTX Properties of the System H_2O-CO_2. *Ph.D. Dissertation*, Virginia Polytechnic Institute and State University .

Price, L. C., 1981. Methane solubility in brines with application to the geopressured resource. *Proceedings of the 5th Geopressured and Geothermal Energy Conference 5, 205-214*.

Ramboz, C., Schnapperd, D., and Dubessy, J., 1985. The *P-V-T-X-*fO_2 evolution of CO_2—CH_4—H_2O-bearing fluid in a wolframite vein: Reconstruction from fluid inclusion studies. Geochimica et Cosmochimica Acta 49, 205-219.

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