A Sorption Study on the Effect of Partial Liquid Saturation of Supercritical CO2 on Clay and Organic-Rich Shales

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I. ABRACT

Rocks, specially shales have heterogeneous mineralogy. We anticipate sorption to be dependent on the association of the pores with the various shale constituents. Furthermore, since shales are expected to have varying levels of water or brine, the water-imbibed shales are better representatives of their natural conditions. However, to date, almost all sorption studies have been performed in the dry state. The purpose of this study is to (1) determine the relative affinity of water and hexane vapors in shales and siltstones during sub-critical adsorption; (2) the sorption capacity of illite clay and organic-rich shale samples in dry and in water-imbibed states during supercritical CO_2. We find that water vapor sorption can be related directly with clay content while hexane vapor is sorbed more in the organic pores. Organic matter pores also play a crucial role in retaining the supercritical CO_2 sorption capacity even in the water-imbibed shales. The rate of sorption is reduced substantially in the presence of water due to the much lower diffusion coefficient of CO_2 in liquid water than that of its gas state. Our findings can improve the current understanding of fluid storage mechanism in partially water-saturated shales for hydrocarbon production and CO_2 sequestration applications.

II. INTRODUCTION

Porous rocks are classified as water- or oil-wet when the surface of their pores is mainly hydrophilic or hydrophobic. In order to differentiate between the water- and oil-wetting pores in shale rocks and to quantify their corresponding total surface, subcritical isotherms of water, hexane and nitrogen vapors in various OM-rich shales were measured. The BET method is used to calculate specific surface area. In its linear form, the BET isotherm equation is:

$$p/p\uparrow 0 \ /(1-p/p\uparrow 0 \ )$$
$$n\downarrow p \ = 1/c \times n\downarrow m \ + c$$
$$= 1/c \times n\downarrow m \ p/p\uparrow 0$$

C=BET constant;

$$p\uparrow 0$$ =saturation pressure

Our results show that water vapor water vapor can act as a selective adsorptive for shales by preferentially probing hydrophilic pores (illite pores), whereas hexane adsorbs in both hydrophilic and hydrophobic pores (OM pores) .

In the first part of this study, the presence of other fluid, such as liquid water is ignored in the experimental assessment of sorption in shales. Since OM pores are potentially hydrophobic as found earlier, those unoccupied OM pores in water-imbibed shales may facilitate sorption of supercritical gases. Supercritical CO_2 sorption isotherms were determined experimentally for the organic-rich shale and illite clay samples in dry and water-imbibed conditions. The kinetics of the sorption was also studied by performing a PTA based study on the time profile of pressure associated with the progression of sorption in the samples.

III. METHODOLOGY & SAMPLES

- **Samples**

For subcritical nitrogen, water vapor and hexane analysis, we used 8 upper and lower Bakken shale samples and 4 middle Bakken siltstone samples with mineral compositions as listed below.

Sample		Mineralogy(wt. %)				OM Properties		
		Carb	Silic	Pyrite	Clay	TOC (wt.%)	HI	Tmax(°C)
Siltstone	1	50	45	0	5	n/a	n/a	n/a
	2	46	37	2	15	n/a	n/a	n/a
	44	20	64	0	16	n/a	n/a	n/a
	3	32	46	2	20	n/a	n/a	n/a
Shale	LG	11	68	4	17	14.4	508	429
	U13	10	75	1	14	6.2	331	445
	U14	10	64	3	23	12.9	401	444
	U5	14	58	1	27	13	377	444
	U7219	2	65	3	30	16.1	556	-
	U11005	9	57	3	31	12.4	131	-
	U16	9	57	1	33	15.1	395	443
	U1	12	36	2	50	10	373	445

Carb:Calcite +Dolomite+Siderite; Silic:Silica+K-feldspar+Plagioclase;n/a:Not applicable;'-':not measured;L#,U#:Lower amd Upper Bakken shale

We used three samples for supercritical CO_2 sorption analysis: Illite clay from the Clay Mineral Society and two organic-rich shales from the Bakken formation belonging to the oil (BK1) and gas (EPU119) thermal maturity windows.

Sample	XRD Mineralogy (wt.%)				ROCK-Eval TOC	Thermal Maturity	BET SSA		
	Illite	Silicates	Carbonate	Pyrite			N_2	H_2O	C_6H_{14}
Illite	100	-	-	-	-	-	25.1	47.5	24.2
BK1	25	62	10	3	12.5	0.8	2.2	9.1	18.2
EPU119	34	59	6	1	11	3.0	22.8	11.2	21.2

- **Methodology**

For subcritical nitrogen, water vapor and hexane analysis, adsorption and desorption isotherms were measured with a Micromeritics ASAP2020 analyzer. Nitrogen isotherms were recorded at liquid nitrogen boiling temperature (-197.5°C), whereas water and hexane vapor isotherms were recorded at ambient lab temperature (21°C to 23°C).

We designed a manometric apparatus for the supercritical sorption experiment as shown below. A tube with a plunger valve is also designed to allow for forced imbibition of water in samples. The material balance and CO2 equation of state proposed by Span and Wagner (1996) were used for the evaluation of isotherms.
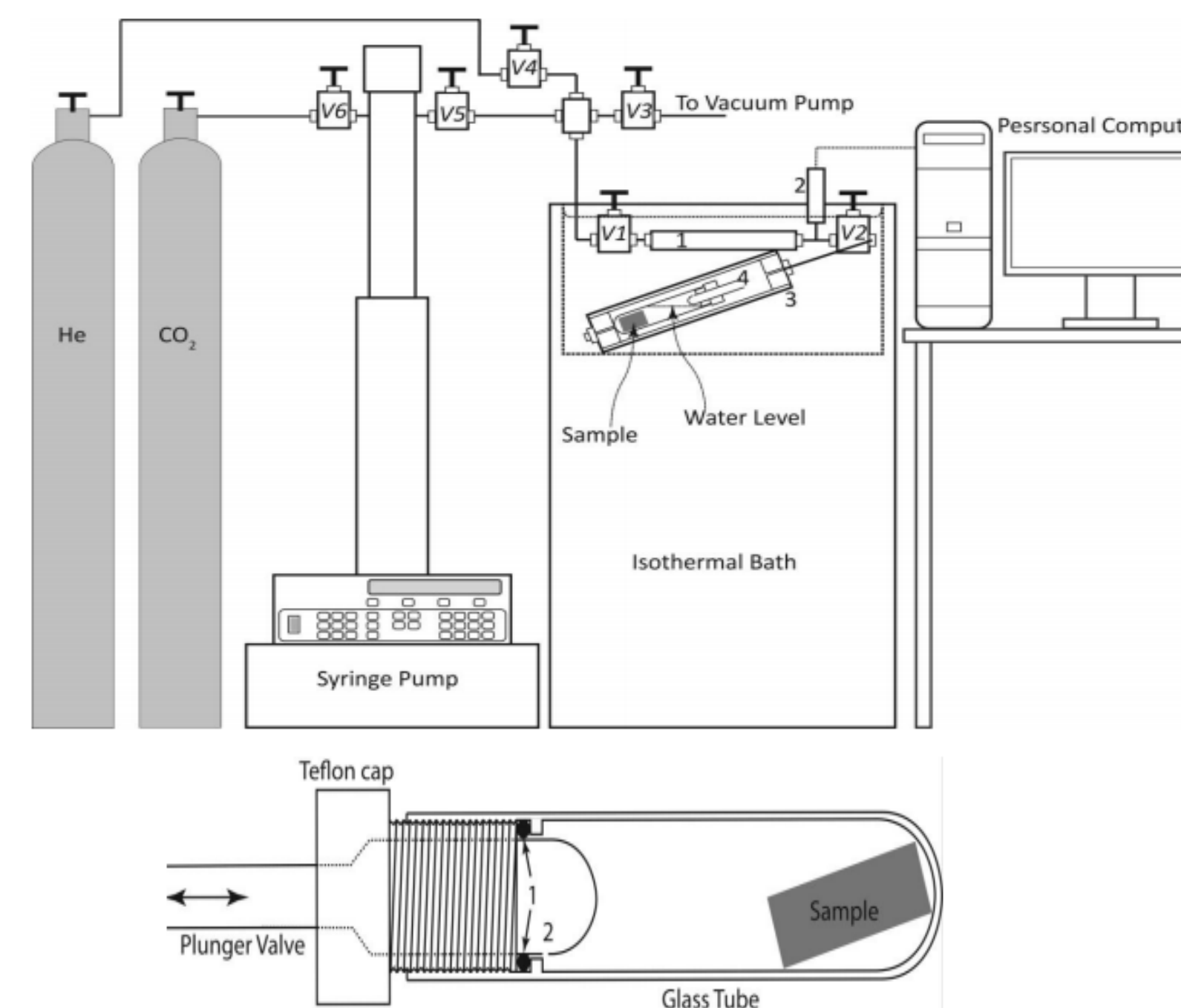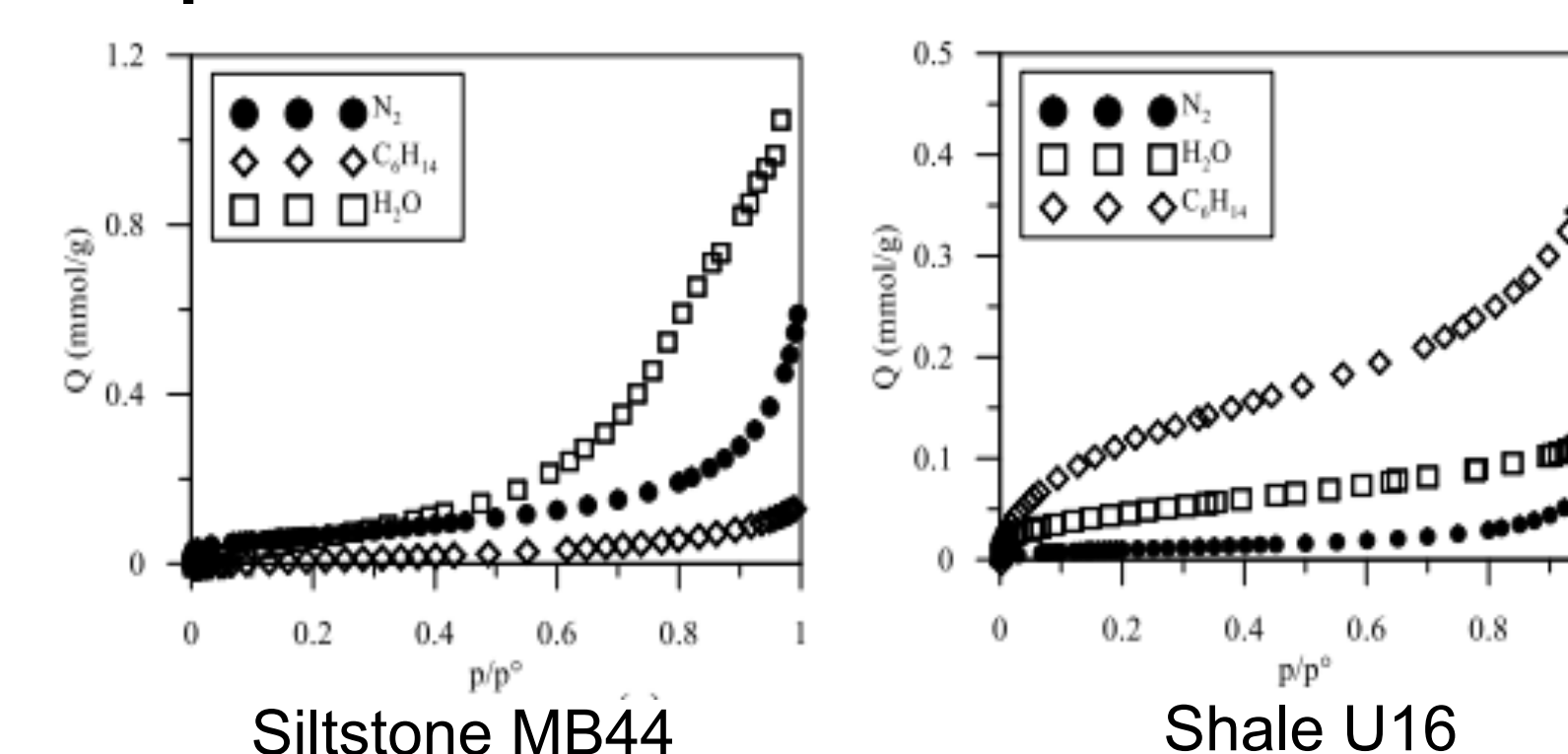

IV. RESULTS

- **Water, Hexane and Nitrogen Isotherm Derived BET SSA**

	Siltstone				Shale							
	1	2	3	44	U1	U5	U13	U14	U16	LG	7216	11005
H2O	1.4	5.6	7.0	5.8	17.0	8.0	4.1	6.2	8.3	6.9	11.2	8.4
C6H14	1.3	4.5	6.0	6.0	11.6	11.6	12.6	11.6	12.6	19.3	27.8	35.1
N2	1.3	4.0	5.8	5.9	2.2	1.2	1.0	0.9	1.0	2.4	3.5	17.6

- **Nitrogen(77k), hexane(298k) and water (298k) isotherms for siltstone sample MB44 and shale sample U16.**

Siltstone MB44   Shale U16

- **Correlation between sample clay content and nitrogen(a), hexane(b) and water(c) SSA results.**
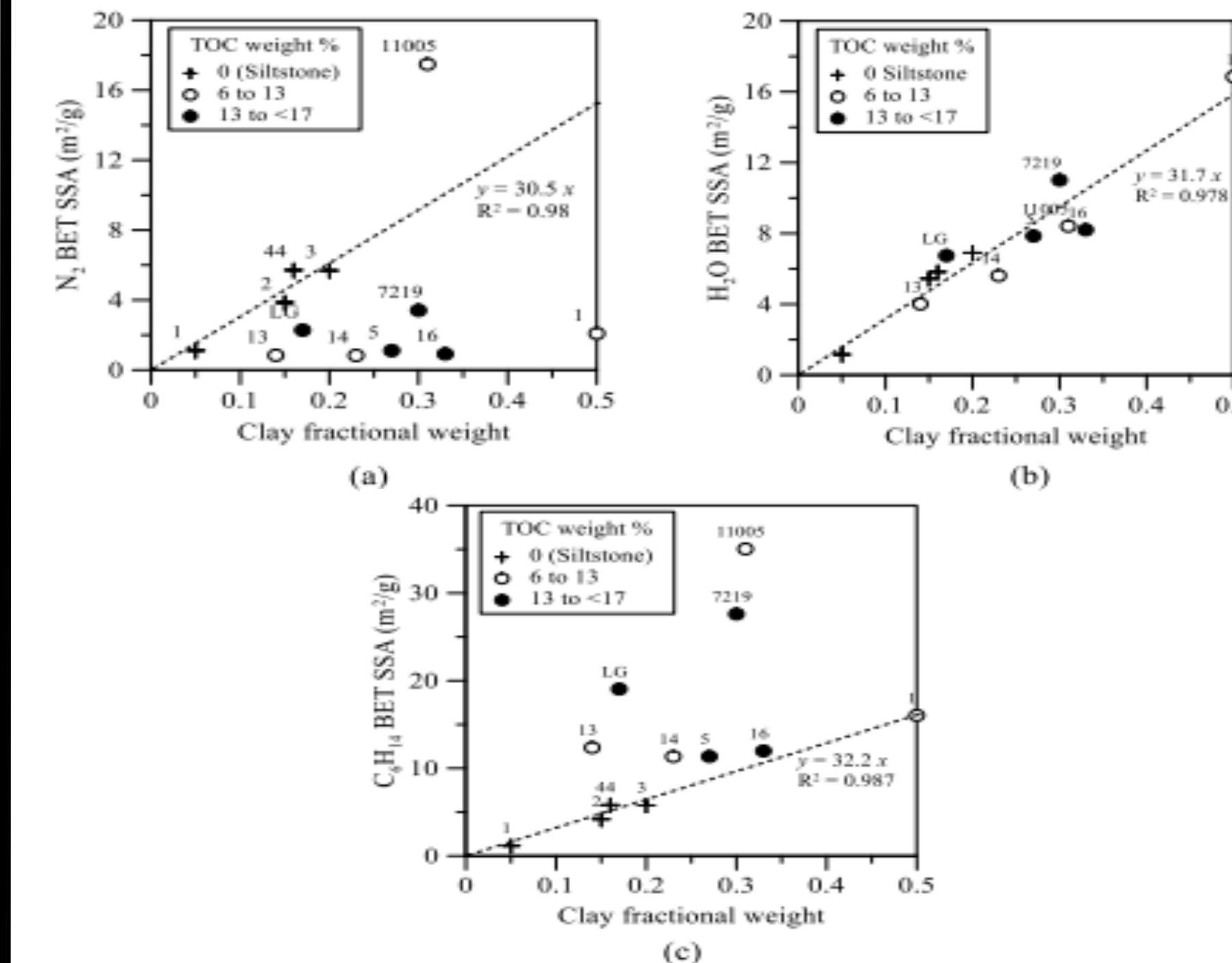
- **Sorption capacities comparisons of BK1 and clay samples in their dry and water-imbibed conditions(a) and two shale samples in their dry and water-imbibed states(b)**
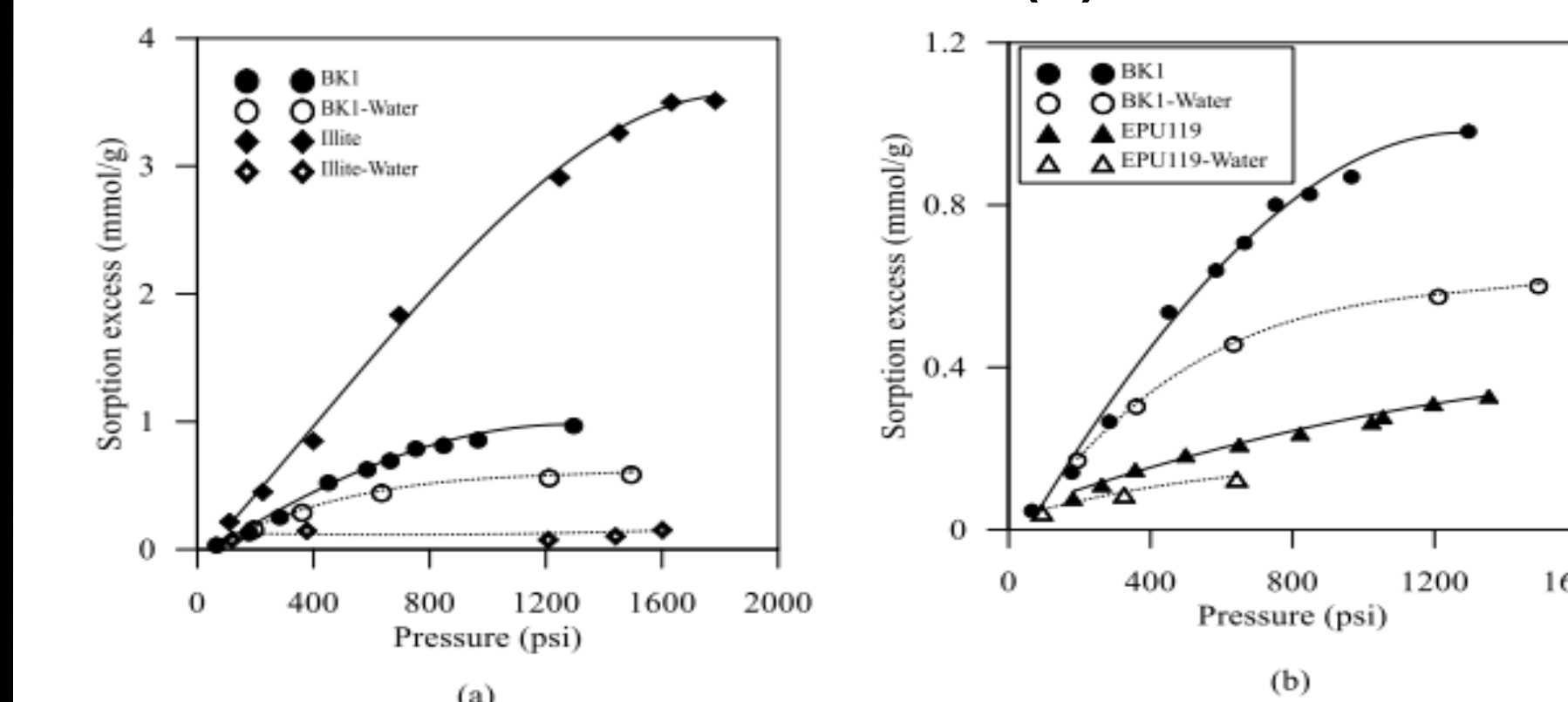
V. CONCLUSIONS

- We quantify hydrophilic and hydrophobic pores in shales using select adsorptives.
- Water-imbibed shales do have sorption capacity for supercritical CO_2
- Presence of water inhibits CO_2 sorption in the clay constituents but not in OM pores.
- Supercritical CO_2 sorption in water-imbibed organic-rich shales suggested the possibility of CO_2 sorption from its dissolved state in water.

References
Kumar,S.,Prasad,M., and Pini,R. 2015. Selective Adsoprtives to Study Pore Structure and Wetting Behavior of Self-resourcing Shales. SPWLA 56th Annual Logging Symposium. SPWLA-2015-EEE
Nandy,D.,Sonnenberg,S.A. and Humphrey,J.D 2015. Factors Controlling Organic-Richness in Upper and Lower Bakken Shale, Williston Basin:An Application of Inorganic Geochemistry. AAPG Annual Convention & Exhibition.10775
Span,R.,Lemmon,E.W.,Jacosen,R.T., Wagner,w., and Yokozeki,A.2000. A reference equation of state for the thermodynamic properties of nitrogen for temperature from 63.151 to 1000k and pressures to 2200 Mpa. Journal pf Physical and Chemical Reference Data, 29(6),1361-1433