

# The effect of wettability on the amount of adsorbed fluid and capillary condensation pressure in nanoporous materials

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**Abstract.** Understanding the effect of wettability on the confined phase behavior of fluids in nanoporous media is essential for numerous applications, such as hydrocarbon production, carbon dioxide sequestration, and gas storage. The present study examines the impacts of hydrophilicity and hydrophobicity of the solid surfaces of MCM-41 (Mobil Composition of Matter No. 41) materials on ethane adsorption. The wettability of the originally water-wet MCM-41 samples was altered to oil-wet conditions using hexamethyldisilazane (HMDS). Adsorption isotherms of ethane in the original and modified MCM-41 samples were measured at two different pore sizes of 80 and 100 Å and varying temperatures employing a gravimetric apparatus. The results show that ethane was adsorbed more onto the hydrophilic nanoporous materials due to the stronger adsorption forces before capillary condensation. They also indicate that the mass variation of the adsorbed ethane between the hydrophilic and hydrophobic materials was notable in the smaller pore size. In addition, the capillary condensation pressures of ethane in the hydrophobic samples were slightly higher than the hydrophilic ones. The effect of wettability on the vapor-liquid phase transition process of confined ethane became more significant with increasing temperatures. The findings from this study considerably enrich the current understanding of the impact of wettability on the adsorption behavior of fluids and the confinement-induced phase transition characteristics in nanoporous materials possessing different surface chemistry.

## 1 Introduction

It is well known that wettability significantly impacts the relative permeability, electrical properties, and saturation profiles of fluids in subsurface geological formations [1]. The influence of wetting conditions on these attributes is paramount for determining the displacement of fluids in porous media [2,3]. Therefore, understanding the effect of wettability is essential for various industrial and scientific applications, including hydrocarbon production from shale and tight reservoirs [4], carbon dioxide sequestration [5], and underground hydrogen storage [6,7]. However, its impact on the phase behavior of fluids in unconventional reservoirs, unlike conventional ones, remains poorly understood and warrants more in-depth investigations.

Numerous studies presented in the literature have reported that the confined phase behavior of fluids in nanoporous media differs from their bulk counterparts [8,9]. For example, the vapor-liquid phase transition process in nanometer-sized pores, called *capillary condensation*, occurs at lower pressures than in bulk spaces in isothermal systems [10–12] and higher temperatures in isobaric systems [9,13,14]. In addition, the pressure-temperature (P-T) phase diagrams of fluids in nanopores are shifted to below those in bulk due to the confinement effect [15–17].

On the other hand, the literature investigating the impact of wettability on the confinement-induced phase behavior of fluids is scarce. Lowry and Piri [18] examined the effect of surface chemistry on the confined phase behavior of ethane in three different types of nanopores, namely face-centered cubic, disordered carbon, and amorphous silica, using grand canonical Monte Carlo (GCMC) models. Their results showed that the critical temperature of ethane in the amorphous silica was higher than in the disordered carbon. They attributed this phenomenon to the weaker intermolecular forces between ethane and carbon. In another study, Zhao and Lu [19] measured the adsorption isotherms of benzene in hydrophilic and hydrophobic nanoporous materials. They concluded that benzene condensed at a much lower pressure in the hydrophilic sample than the hydrophobic due to pore configuration rather than surface chemistry. Consequently, the effect of wettability on capillary condensation pressure remains unclear and requires further research.

The International Union of Pure and Applied Chemistry (IUPAC) [20] reported that the wetting conditions of an adsorbent considerably influence the shape of the adsorption and desorption isotherms. In other words, the wetting phase is expected to absorb more onto the pore walls, directly affecting the amount of adsorbed fluid in nanoporous media. Sen et al. [21] studied the behavior of liquid hydrocarbons, including n-heptane,

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pentane, and their mixtures, in shale organic pores using Molecular Dynamic (MD) simulation. They observed more layer-like adsorption of the heavier hydrocarbon, i.e., n-heptane, in organic pore surfaces. However, the experimental data from Zhao and Lu [19] on adsorption isotherms of benzene in hydrophilic and hydrophobic nanoporous samples indicated that benzene was adsorbed more onto the water-wet materials. Therefore, more studies are needed to fully understand the effect of wettability on the adsorption behavior of fluids in nanoporous materials.

The present study endeavors to improve the current understanding of the impact of wettability on the thermodynamic properties of fluids confined in nanoporous media. We employ an upgraded gravimetric apparatus to experimentally measure the adsorption isotherms of ethane in hydrophilic and hydrophobic MCM-41 samples. As the condensation of a gas does not occur above the critical temperature, i.e., 32.2 °C for ethane (see Fig. 1), and ethane can attain a supercritical-like state in nanopores at a much lower temperature than the critical point [14], the tests were conducted at three temperatures of -20, -10, and 0 °C and two pore sizes of 80 and 100 Å. MCM-41 is inherently water-wet, and a wettability alteration process was performed using hexamethyldisilazane (HMDS) to alter its wettability to hydrophobic conditions. The original and modified materials were thoroughly analyzed utilizing various techniques to confirm their wetting states. The results from this work provide valuable insights into the effect of wettability on the amount of gas storage in nanoporous materials as well as the confinement-induced phase transition pressures of fluids.

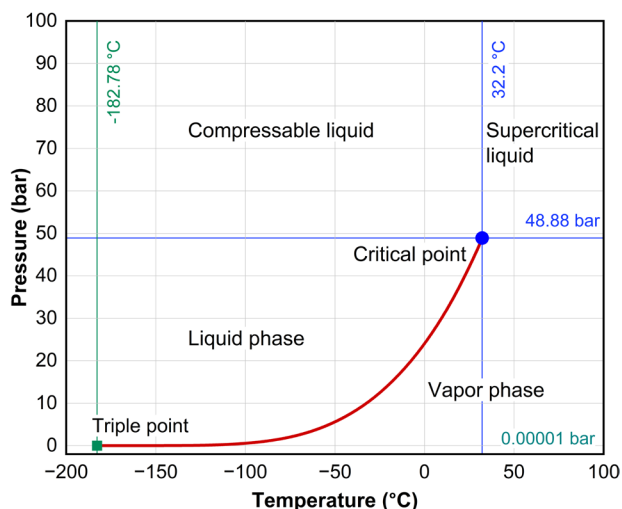


Fig. 1. Thermodynamic phase diagram of ethane.

The remainder of the paper is structured as follows. Section 2 describes the materials and methods employed in this study. It also presents the procedure of wettability alteration and the isothermal measurement technique. The results of adsorption isotherms obtained for hydrophobic and hydrophilic samples are provided and discussed in Section 3. Finally, Section 4 provides conclusions and suggestions for future studies.

## 2 Materials and Method

### 2.1 Materials

This study utilized gaseous ethane (from Airgas) with a purity of 99% as the testing fluid. Its confined phase behavior was examined in hydrophilic and hydrophobic nanoporous materials with similar pore diameters and shapes. The MCM-41 samples with 80 and 100 Å pore sizes (from Glantreo, Ltd) were used as adsorbent materials. MCM-41 (Mobil Composition of Matter No. 41) is a well-known synthetic nanoporous material possessing pores with hexagonal shapes and well-controlled sizes. The original samples were modified with hexamethyldisilazane (HMDS) (from Thermo Fisher Scientific) to attain hydrophobic counterparts. A detailed modification procedure is presented in the literature [22,23]. Fig. 2 shows the schematics of the reaction governing the wettability modification process. The cleaned MCM-41 samples possessing the silanol [-Si(OH)] functional groups were treated with HMDS at 55 °C for 20 hours to obtain hydrophobic materials with the trimethylsilyl (TMS) groups [-Si(CH<sub>3</sub>)<sub>3</sub>] present on the surface.

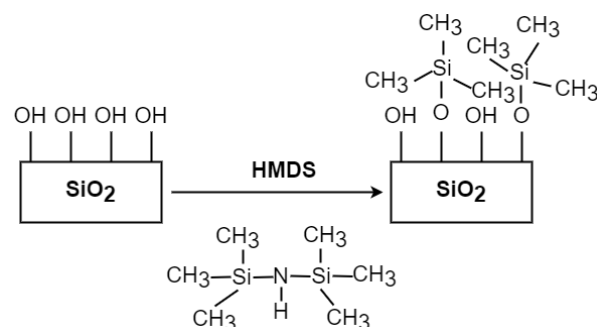
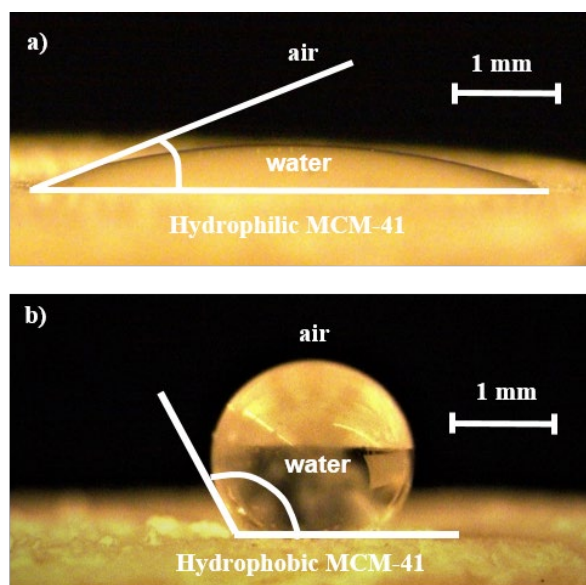


Fig. 2. Reaction of MCM-41 sample with HMDS to change its wettability from hydrophilic to hydrophobic.

The wetting states of the original and modified MCM-41 materials were determined by measuring the contact angles of water droplets on tablets of compacted samples. As shown in Fig. 3 (a), water was adsorbed immediately into the hydrophilic porous media, exhibiting a contact angle consistently less than 90°. On the other hand, the water droplet possessed a spherical shape on the surface of the hydrophobic material and showed a large contact angle, see Fig. 3 (b). It should be noted that the surface roughness due to the compacting process of the samples might affect the accuracy of the contact angle measurements in this study.

The average pore sizes of the hydrophilic and hydrophobic samples were determined by the Barrett-Joyner-Halenda (BJH) [24] technique via adsorption and desorption isotherms of nitrogen at 77 K. The BJH method employed the Kelvin equation [25] to relate the relative pressure ( $P/P_0$ ) at which capillary condensation of nitrogen occurs to the radius of the pore ( $r$ ). The results of the measured pore sizes and the amount of each sample used are tabulated in Table 1. Although the pore size of the hydrophobic MCM-41 (100 Å) sample was slightly

reduced compared to the hydrophilic after the modification process, its effect on the measurement of adsorption isotherm was negligible [26,27].



**Fig. 3.** Contact angles of a) water and hydrophilic MCM-41 sample and b) water and hydrophobic MCM-41 sample.

**Table 1.** Nanoporous material characteristics.

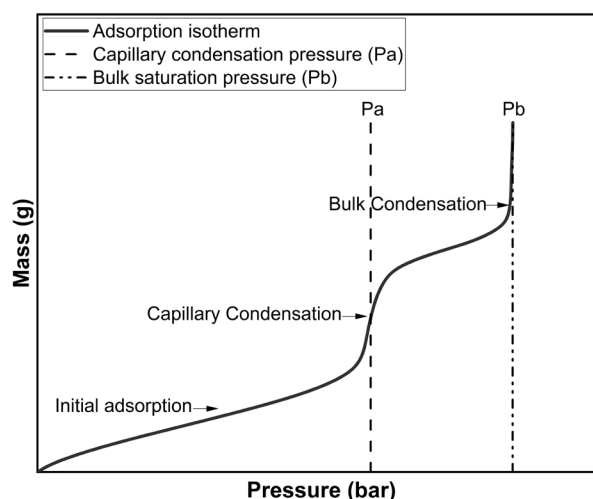
MCM-41 sample (Å)	Hydrophilic MCM-41		Hydrophobic MCM-41	
	Pore size (nm)	Mass (g)	Pore size	Mass (g)
80	7.83	6.52	7.83	7.71
100	9.56	6.12	9.54	8.32

## 2.2 Experimental Setup and Procedure

We employed a patented nano-condensation apparatus [28,29] to experimentally probe the confined phase behavior of ethane in nanoporous media. The apparatus measures the adsorption isotherms of fluids by directly estimating the amounts of fluid adsorbed onto the pore wall and the corresponding bulk pressures under constant temperatures. The results from the literature utilizing this experimental setup demonstrate remarkable precision and reliability [10,14,30]. A comprehensive description of the apparatus can be found in the literature [28,29].

The hydrophilic and hydrophobic MCM-41 samples with two different pore diameters were packed into four titanium sample holders. They were suspended in an environmental chamber through the balances situated atop. Tubing and automatic valves connected the core holders inside the chamber to the pressurized gas cylinder and the vacuum pump located outside the system. Pressure transducers were utilized to measure the pressure inside the sample holders. The entire setup underwent a 48 hours-vacuum process before conducting any experiments.

The apparatus measures mass-pressure adsorption isotherms by introducing small doses of fluid from the gas cylinder into the core holders containing the nanoporous material. The automatic Vindum valves open and close briefly to allow fluid injections. This process gradually increases the mass of the fluid and pressure inside the sample holders. A LABVIEW computer program was set up to record all data points. As shown in Fig. 4, the collected data on mass and pressure constitute an isotherm, starting from the initial adsorption phase to capillary condensation and finally leading up to bulk condensation.



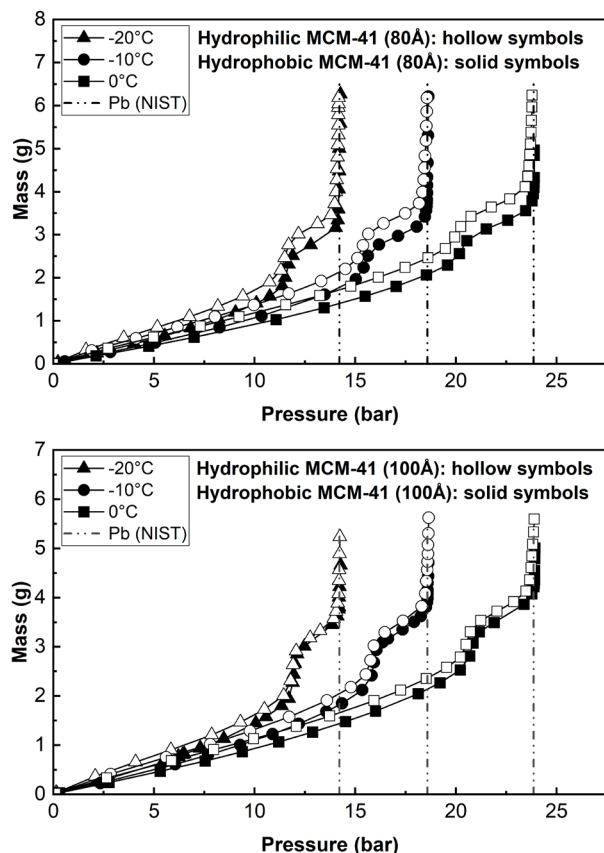
**Fig. 4.** Schematic diagram of a model adsorption isotherm.

## 3. Results and Discussion

This section presents the results of the effect of wettability on the confined phase behavior of ethane in hydrophilic and hydrophobic nanoporous materials. Fig. 5 shows the experimentally measured adsorption isotherms of ethane in hydrophilic and hydrophobic MCM-41 samples with two pore sizes of 80 and 100 Å at three different temperatures (-20, -10, and 0 °C). These isotherms were carefully examined to draw inferences on the impact of wetting conditions on the amount of adsorbed fluid and capillary condensation pressure.

The results show that the wettability affects the amount of adsorbed fluid in nanoporous materials. It is evident from the adsorption section of the isotherms that the increase in the adsorbed mass is more significant in the case of hydrophilic samples than in the hydrophobic ones. In other words, more ethane was adsorbed onto the surfaces of the hydrophilic nanopores than the hydrophobic counterparts. This is attributed to the stronger adsorption forces between the non-polar ethane molecules and the polar hydrophilic surfaces of the solid [31]. It is noticed that the physical adsorption forces are the van der Waals forces [31]. The interactions between non-polar and polar molecules are called Debye (dipole-induced dipole) forces. Those between two non-polar molecules are London dispersion (instantaneous dipole-induced dipole) forces. Dispersion interactions were found to be the weakest of the intermolecular forces [31].

The weak dispersion interactions between ethane and the hydrophobic pores resulted in less ethane stored in the oil-wet nanoporous materials.

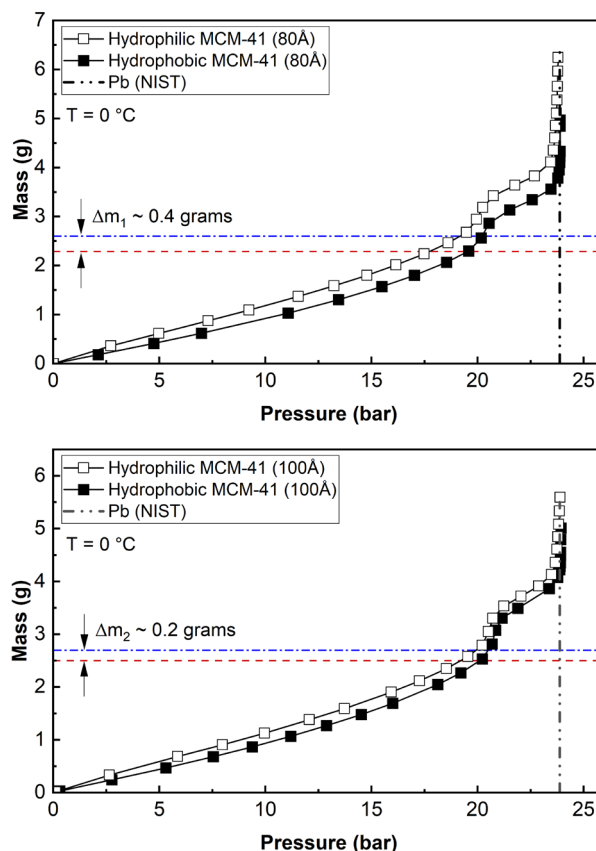


**Fig. 5.** Experimentally measured adsorption isotherms of ethane in hydrophilic and hydrophobic MCM-41 (with 80 and 100 Å pore diameters) samples.

Fig. 6 compares the mass of ethane stored in the hydrophilic and hydrophobic MCM-41 samples of similar pore sizes at 0 °C before approaching the capillary condensation. The variation in mass between the hydrophilic and hydrophobic samples ( $\Delta m_1$ ), in the case of 80 Å pore diameter, was approximately 0.4 grams, whereas the difference between the two samples with 100 Å pore diameter ( $\Delta m_2$ ) was nearly 0.2 grams. Similarly, the variations in the amount of adsorbed ethane between different wetting states were generally more notable in the case of smaller pore size at all experimental temperatures (see Fig. 5). The distinct mass variations in the 80 Å pore size indicated the stronger short-ranged intermolecular forces.

Interestingly, during the initial adsorption process, the variations in the adsorbed mass of ethane were insignificant in nanoporous materials with different pore sizes possessing similar wetting conditions. As shown in Fig. 7, the amount of fluid adsorbed onto the surfaces of hydrophilic samples with 80 and 100 Å pore diameters almost overlapped. Likewise, as evident from the adsorption isotherms, the rates of mass increase for hydrophobic samples of different pore sizes were nearly identical before approaching the capillary condensation.

This observation confirmed the significant impact of wettability rather than pore dimensions on the amount of adsorbed fluid in nanoporous media.

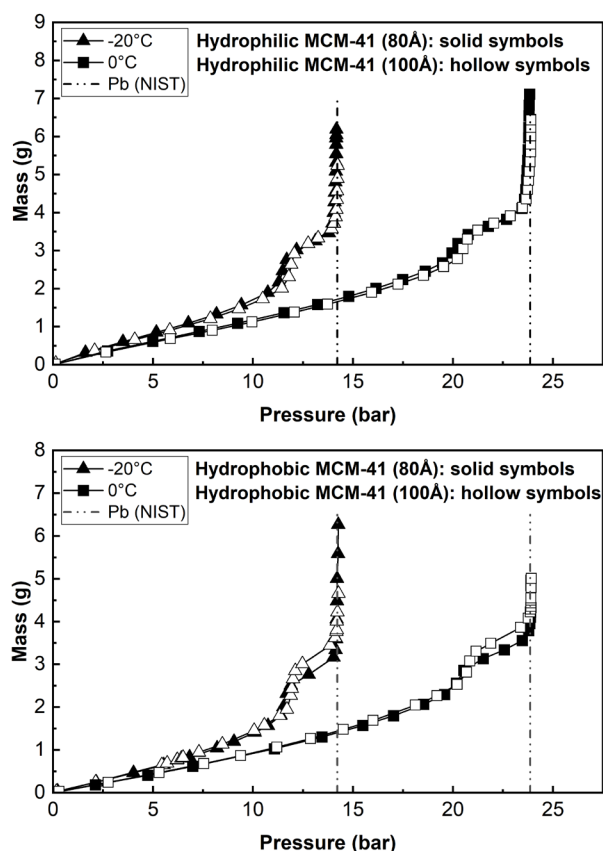


**Fig. 6.** The mass variation of adsorbed ethane in nanoporous materials with different wetting states.

In addition, capillary condensation pressures of ethane were calculated to examine the effect of wettability on the confined phase behavior of fluids in nanoporous media. The condensation of fluids under confinement was specified as the abrupt change in mass at intermediate pressures on the measured adsorption isotherms (see Fig. 4). The inflection point of this sudden change was defined as capillary condensation pressure ( $P_a$ ) in the literature [11,29].

Table 2 provides experimentally-measured capillary condensation pressures of ethane in the hydrophilic and hydrophobic materials denoted as  $P_{a1}$  and  $P_{a2}$ , respectively. As shown in Table 2,  $P_{a2}$  was slightly higher than  $P_{a1}$ , irrespective of temperatures and pore sizes. For example,  $P_{a1}$  at -20 °C in the 100 Å sample was 11.87 bar, compared to 11.96 bar  $P_{a2}$  at the same experimental conditions. Although the variations between  $P_{a1}$  and  $P_{a2}$  were insignificant, they exceeded the standard error range. The results indicated that the hydrophilic pores became saturated with the liquid-like ethane before the hydrophobic ones, confirming the stronger fluid-solid intermolecular interactions between ethane and the hydrophilic surfaces. In addition, the variations between  $P_{a2}$  and  $P_{a1}$  increased once the temperature rose from -20 to 0 °C for both pore sizes of 80 and 100 Å (see Table 2).

Therefore, the results suggest that the effect of wettability on the capillary condensation pressure becomes more profound with ascending temperatures. However, more experimental data at a broader range of temperatures are needed to further corroborate this conclusion.



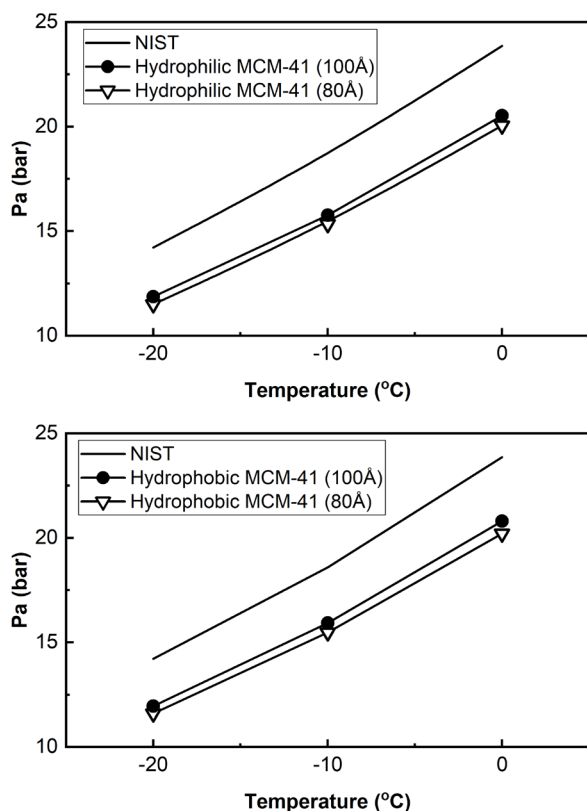
**Fig. 7.** Comparison of the effect of pore size on ADS isotherms of ethane in hydrophilic and hydrophobic MCM-41 (80 and 100 Å) samples.

**Table 2.** Measured capillary condensation pressure ( $P_a$ ) of ethane in (1) hydrophilic and (2) hydrophobic MCM-41 samples.

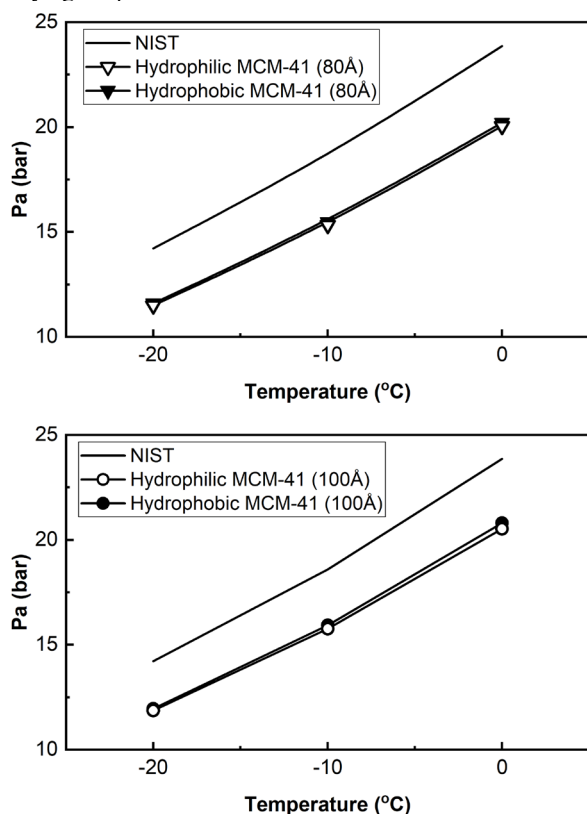
Temperature (°C)	Pore size (Å)	$P_b$ NIST (bar)	$P_{a1}$ (bar)	$P_{a1}$ standard errors (bar)	$P_{a2}$ (bar)	$P_{a2}$ standard errors (bar)	Variation $P_{a2}-P_{a1}$ (bar)
-20	80	14.22	11.50	0.002	11.60	0.002	0.10
-10	80	18.59	15.34	0.016	15.48	0.019	0.14
0	80	23.87	20.05	0.008	20.21	0.039	0.26
-20	100	14.22	11.87	0.005	11.96	0.003	0.09
-10	100	18.59	15.77	0.012	15.93	0.063	0.16
0	100	23.87	20.53	0.010	20.80	0.017	0.27

The vapor-liquid phase transition of ethane in confined spaces occurred at lower pressures than their bulk counterparts under isothermal conditions, which conforms with the observations presented in the literature [9,11,29]. For example, the bulk saturation pressure ( $P_b$ ) of ethane at -20 °C was 14.22 bar, whereas its capillary condensation pressures in the hydrophilic MCM-41 sample with pore sizes of 80 and 100 Å were 11.50 and 11.87 bar, respectively (see Table 2). The effect of confinement on the phase properties of ethane was more profound in the case of small pore size, regardless of the wetting conditions. In other words, capillary condensation pressures of ethane in the 80 Å MCM-41 samples were lower than in the 100 Å samples in both hydrophilic and hydrophobic cases. It is also evident from the results, as shown in Fig. 8, that the vapor-liquid phase transition pressures deviated further away from the bulk saturation values on a pressure-temperature (P-T) phase diagram with decreasing pore sizes.

The effect of wettability on the confinement-induced phase behavior of ethane was less significant than that of the nanoscale pore size. Fig. 8 and Fig. 9 show that the variations of  $P_a$  were more sensitive to the changes in pore dimensions rather than the wettability conditions. In other words, the confined phase behavior of ethane was less affected by the surface's physicochemical properties. This is attributed to the fact that ethane is a light hydrocarbon gas, and the impact of wettability in confined systems mainly depends on the intermolecular interactions between fluids and solids. The adsorption forces become predominant in the cases of fluids with large molecular sizes [32]. Therefore, it is imperative to obtain more experimental data on the confined phase behavior of adsorbates with a wide range of physical properties.



**Fig. 8.** Comparison of the effect of pore size on capillary condensation pressure of ethane in MCM-41 materials at varying temperatures.



**Fig. 9.** Comparison of the effect of wettability on capillary condensation pressure of ethane in MCM-41 materials at varying temperatures.

## 4 Conclusions

This work investigates the effect of wettability on the confined phase behavior of fluids in hydrophilic and hydrophobic MCM-41 mesoporous materials. The wettability of the original hydrophilic MCM-41 samples was modified with hexamethyldisilazane (HMDS) to obtain hydrophobic samples. Adsorption isotherms of ethane were generated using the MCM-41 samples possessing different wetting states with two pore sizes (80 and 100 Å) at three different temperatures (-20, -10, and 0 °C). To this end, an upgraded gravimetric apparatus was employed to directly measure the mass of the adsorbed fluid vis-à-vis variations in the system's pressure. The results suggest that the degree to which wettability affects the amount of adsorbed fluid in nanoporous materials depends on the strength of fluid-solid intermolecular forces. Ethane was adsorbed less onto the hydrophobic surfaces than the hydrophilic ones because of the weaker dispersion interactions. It is also evident that the difference in the amount of adsorbed ethane between the hydrophilic and hydrophobic samples was significant in the smaller nanopores. Furthermore, capillary condensation occurred at lower pressure in the hydrophilic nanopores compared to the hydrophobic counterparts. This variation in capillary condensation pressure between different wetting states increased at higher temperatures. However, the effect of wettability on the confinement-induced phase transition process of ethane was not as remarkable as the impact of pore size. The results from this study provide crucial insights into the effect of different wetting conditions on the phase behavior of fluids confined in nanoporous media.

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