Simple universal Kelvin equation valid in critical point vicinity, external-internal state correction, and their application in understanding of normal pentane capillary evaporation and condensation in mesoporous silica MCM-41

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Abstract. A new simple universal form of the Kelvin equation, which can be used near the gas-liquid phase transition critical point, and the correction of the pressure and density for gas phase fluid outside the porous medium are used for the normal pentane meniscus effective curvature radius calculation at the phase equilibrium in mesoporous silica MCM-41, on the basis of the capillary evaporation and condensation experimental data. Normal pentane is suggested as a promising fluid for characterizing the porosity that can be used even at room temperature.

1. Introduction

Porous media open the new opportunities for science and technology [1-3]. Considering mesoporous ones, we should take into account that these are nanoscale materials. Many methods for studying adsorption-desorption and condensation-evaporation processes in mesoporous media have been developed: traditional techniques (see the review paper [4]), CARS spectroscopy [5,6], NMR study [7], and positron annihilation spectroscopy [8]. The works [9,10] will be used further on in this paper for having the data for n-pentane.

There is a bit of ambiguity in characterizing the situation at the moments of condensation and evaporation. Our treatment is based on the assumption that some of the processes happen in the state of the thermodynamic equilibrium and with hemispherical meniscus geometry. For them we estimate effective meniscus curvature radii on the basis of the experimentally known evaporation and condensation pressures [9,10].

The model that has already been tested with 4 substances (CO$_2$ (Ref. [3] in [12]), N$_2$ [12], Ar (Ref. [16] in [13]), and O$_2$ [13]) will be used for normal pentane in this work. MCM-41 is a controlled pore glass, which means the pores can be treated as almost the same size cylinders. The model consists of the 2 stages: the new Kelvin equation (Refs. [2,3] in [12]) and the state transformation of the gas phase from the center of the meniscus hemisphere to the bulk [12]. Joining the two model stages allows [12] one getting the gas-phase pressure outside the porous medium as a function of the meniscus effective curvature radius at the phase equilibrium inside the pores. Vice versa, one can find the radius as a function of the pressure in bulk. The latter is available in the works [9,10] for several temperatures.
The results produced in this way will be presented in the next section. The works [10,11] also have the results for the n-pentane adsorption in a sample with the pore radius of 1.45 nm. At the same time the authors of [11] conclude (and we agree with them) that the adsorption took place in a supercritical state where our model is not applicable.

2. Results

Normal pentane is a nonpolar fluid. Thus its Tolman’s length [14] should be smaller than the molecule average diameter in the states distant enough from the critical point, to which the scope of this work is limited.

PC-SAFT EOS used in the work [15] behaves in some sense correctly in the instability region and therefore is suitable for handling the ‘light phase’. In the present work, the treatment is limited to stability and metastability regions. Thus the choice of the EOS can be extended to high-accuracy empirical ones. The equation of state of [16] and the phase equilibrium equations of [17] will be chosen further on in this paper.

If we take some spherical meniscus effective curvature radius then using the integral equations (9), (13) in (Ref. [3] in [12]), the equations of state and the parachor equation [18] for pure fluids, the phase equilibriums can be calculated. Pressure outside the pores can be calculated using equations (6-9) of [12]. Fitting it to the measured one [9,10], we can find the radius.

The value 230.93 \( \text{dn}^{\frac{1}{4}} \text{cm}^{\frac{1}{4}} \text{f} \text{mol} \) of [15] will be used for the n-pentane parachor. For the Lennard-Jones potential, the authors will use the parameters [19] \( e_{\text{FF}} = 309.75 \text{K} \cdot k_B \) and \( \sigma_{\text{FF}} = 0.6709 \text{nm} \).

Because it is not quite firmly established [15,20-28] yet, which (if either) of these processes (evaporation and condensation) takes place in the state of the thermodynamic equilibrium, the method used in this work is applied formally to the both of them, giving the possible meniscus radii at the moments of capillary evaporation and condensation (see figure 1). For the condensation branch of the \( r = 2.285 \text{nm} \) sample [9] open symbols are used. The same is for the temperatures, at which the hysteresis is not observed. Solid symbols show the results for the evaporation branch. Pentagons with horizontal lines show the results for the \( r = 2.095 \text{nm} \) sample [10]. For the single available [10] \( 297.95 \text{K} \) isotherm of the \( r = 4.04 \text{nm} \) sample we have the effective curvature radius of 3.51 nm, not shown in the figure 1. The model these results are obtained with, does not take the pore size into account. At the same time, as soon as we know the curvature radius and the average pore radius, we are able to calculate the \( \lambda \)-parameter [15], which is shown in figure 2 by pentagons. The shape of the symbols presented for n-pentane is the same as in figure 1. The \( \lambda \)-parameter of \( r = 4.04 \text{nm} \) sample is shown by a pentagon with a vertical line. Analogous results of [15] are shown by semisolid symbols.

In figure 2 hexagons show the results for \( \text{O}_2 \) of [13] (closed symbols are used for the evaporation branch, otherwise are used open symbols, semisolid symbols show the results of [15] for comparison), rhombi show the similar way the results for \( \text{Ar} \) of (Ref. [16] in [13]) and [15], rounds show the results for \( \text{N}_2 \) of [12] and [15]. Triangles show the results of the works (Ref. [3] in [12]) and [15]. Open triangles show the results published in (Ref. [3] in [12]), where the capillary condensation pressures were taken indirectly from figure 3 of [29]. Closed triangles show the results (Ref. [16] in [13]) by the improved model (Ref. [4] in [12], [12]), where the corrected equations (7), (8) of [12] were used, and also the capillary condensation pressure data were taken from figure 4 of [29]. Semisolid triangles show the results of [15].

3. Discussion

One may notice that the results given by the present model for n-pentane are significantly different from these for the other 4 substances. In [15] this situation is not observed. Thus, we should look at it in detail. The present model requires [12] that the adsorbed layer is sufficiently thick, which is not valid now. This can be mended by adding an extra (accounting for the cylindrical pore wall attraction caused mainly by its oxygen atoms) term \( \mu_{f,S} \) to \( \mu_f \) [12]:
\[ \mu_f = \mu_{f,S} + \frac{\mu_{f,sph} + \mu_{f,ctl}}{2}, \]  

where

\[ \mu_{f,S} = -\alpha \frac{3\pi}{2(R + \sigma_{SF}/2)^3}, \]  

\[ \alpha = (2\pi/3)N^2_A(n_S\varepsilon_{SF}\sigma_{SF}^6 - n_L\varepsilon_{FF}\sigma_{FF}^6). \]  

Here \( N_A \) is the Avogadro number, \( n_S, n_L \) are the silica bridging oxygen atoms and liquid molecules molar concentrations, respectively; \( \varepsilon_{SF} \) and \( \sigma_{SF} \) are the bridging-oxygen-fluid, \( \varepsilon_{FF} \) and \( \sigma_{FF} \) are the fluid-fluid Lennard-Jones potential parameters, respectively, \( R + \sigma_{SF}/2 \) is used instead of the pore radius \( R \) to account for the solid atom center shift from the pore surface. We don’t take into account the attraction of non-bridging oxygen atoms of silica because their actual amount is not well known.

**Figure 1.** Spherical meniscus effective curvature radius at the moment of normal pentane capillary evaporation and condensation in MCM-41 as a function of the temperature.

**Figure 2.** \( \lambda \)-parameter as a function of the temperature.
We may adopt the Lennard-Jones parameters of the bridging oxygen used in many molecular dynamics simulations [30–32]: ε_{SS} = 230 K·k_B, σ_{SS} = 0.27 nm. Upon application of the Lorentz-Berthelot combining rules we obtain ε_{SF} = 266.9129 K·k_B, σ_{SF} = 0.47045 nm.

If we look at two terms in the brackets in (3), we can see that the first one responsible for interaction of the gas phase fluid with the silica is $2.93 \times 10^{-72}$ J·mol·m$^3$ and the second one responsible for the interaction of the gas with the liquid phase fluid varies from $3.25 \times 10^{-72}$ J·mol·m$^3$ (for the lowest density achieved at 298 K) to $3.47 \times 10^{-72}$ J·mol·m$^3$ (for the highest density achieved at 258 K). The difference between the two terms in (3) is much less than their values. The interaction with the silica oxygen atoms appears to be weaker than the fluid-fluid one. At the same time, as far as we are not accounting for the stronger interaction with the non-bridging oxygen atoms concentrated at the pore surface, we cannot say with much certainty, which of the interactions is actually stronger in the $\mu_{f,s}$ term. We can only deduce that $\mu_{f,s}$ value should be relatively small. Therefore neglecting it in the present work results is justified. On the other hand, the weak pore walls attraction makes multiple layer adsorption at the phase equilibrium (with the hemispherical meniscus) questionable. Hence the curvature radius should be approximately equal to the pore radius, this fact making n-pentane an alternative to nitrogen for assessing the average pore radius even at room temperature.

4. Summary
On the basis of the available capillary evaporation and condensation data [9,10], the spherical meniscus effective curvature radius at the moment of the normal pentane possible thermodynamic equilibrium capillary evaporation/condensation in MCM-41 and the $\lambda$-parameter have been calculated for several temperatures. The $\lambda$ values we have obtained for n-pentane are significantly closer to zero than those we had got for other fluids, which is not observed in [15]. The results of this work are justified by the fact that the attraction of the fluid molecule by the silica wall is of almost the same magnitude as the attraction by the adsorbed or liquid-phase fluid. Normal pentane is suggested as a prospective medium for characterizing the porosity.

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