Isotherms, Isobars, Thermodynamics and Kinetics of a Methane-Shale Adsorption Pair Under Supercritical Condition: Implications for Understanding a Shale Gas Storage Mechanism

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Abstract

Understanding the gas-shale interactions including gas adsorption capacity and adsorption kinetic process is of profound significance for predicting the in-situ gas content, evaluating gas flow behavior and understanding shale gas storage mechanism. Till date, numerous experimental results for gas adsorption capacity of shale have already been reported in different countries, but there is paucity of published data systematically investigating the gas adsorption isotherms, isobars, thermodynamics and kinetics of organic-rich shale. To this end, this research work selects supercritical methane and organic-rich shale as adsorbate-adsorbent pair to investigate supercritical methane-shale adsorption behavior. The isotherms, isobars and kinetics of methane-shale adsorption pair are measured at temperatures of 303 K, 323 K, 343 K and 363 K by using a volumetric experimental setup. Then, the Langmuir, Brunauer-Emmett-Teller (BET) and Dubinin-Astakhov (D-A) models are used to interpret measured isotherms, and the Unipore Diffusion (UD), Bidisperse Diffusion (BD) and Two Combined First-Order Rate (TCFOR) models are used to interpret the adsorption kinetics data. Instead of using coefficient of determination (R2 or adjusted R2), this work used the corrected Akaike's Information Criterion (AICc) for model selection, and to the best of our knowledge, this is the first time the AICc

is applied in gas-shale interactions study. It is found that the D-A model is more suitable for adsorption isotherms, and the TCFOR model is more appropriate for adsorption kinetics study. Additionally, for methane-shale adsorption under supercritical condition, the fugacity is of great significance in evaluating thermodynamic properties including isosteric heat of adsorption (qst), enthalpy change (ΔH), entropy change (ΔS) and Gibbs free energy change (ΔG). These thermodynamic properties show strong dependence on adsorption amount or temperature, and suggest that supercritical methane adsorption on organic-rich shale is a process of physisorption, exothermic and spontaneous. Further, the kinetics parameters extracted from kinetics curves suggest that the methane adsorption at each pressure step is a two-stage process. At lower pressure steps, the faster macropore diffusion dominates the two-stage adsorption process, while at higher pressure steps slower micropore diffusion dominates.