ON DERIVING THERMODYNAMIC PROPERTIES FROM THE ADSORPTION ISOTHERM

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Introduction

The reliable estimation of derived thermodynamic properties such as the isosteric heat of adsorption and the adsorbed phase heat capacity is one of the most important corner stones for realistic design and simulation of different adsorption processes. Moreover, such properties provide significant information about the physical characters of specific adsorption systems, including the adsorbent surface heterogeneity and adsorbate-adsorbate lateral interactions [1,2].

The isosteric heat of adsorption is typically estimated by applying the Clausius-Clapeyron equation to the adsorption isotherm data [1]. The temperature dependence of the isosteric heat of adsorption is conventionally ignored because of the usually observed linearity of the pressure logarithm versus the reciprocal temperature. As a result of this assumption, the adsorbed phase heat capacity is conventionally approximated from the gas phase heat capacity. Recent analyses [2-4] showed that some adsorption conditions can cause slight temperature dependencies of the isosteric heat of adsorption, resulting in relatively considerable deviations between the adsorbed and gas phase heat capacities.

This study attempts to evaluate this dependence using a statistically-optimized regression method for smoothing the experimental data obtained for the alkane series C_1 to C_7 over a wide range of temperatures and pressures. Adsorption equilibria of methane, ethane, propane, n-butane, n-pentane, n-hexane and n-heptane on BAX activated carbon were measured and analyzed; and the corresponding isosteric heats of adsorption and adsorbed phase heat capacities were predicted under different adsorption conditions.

Experimental

Adsorption equilibria for methane, ethane, propane, n-butane, n-pentane, n-hexane and n-heptane on BAX activated carbon were measured gravimetrically using a VTI Integrated Microbalance System driven with National Instruments LabView hardware and software. A summary of the experimental conditions is shown in Table 1. Prior to each isotherm measurement, the activated carbon was regenerated at 523 K for 2 hrs under a vacuum of less than

1×10^{-5} torr. Methane, ethane and n-butane were all CP-grade and obtained from National Welders; propane was CP-grade and obtained from Matheson Gas Products, Inc.; n-pentane and n-heptane were 99+% pure and obtained from Alfa AESAR; and n-hexane was 99+% pure and obtained from Sigma Chemicals Company. All the adsorbates were used as received. The BAX activated carbon was obtained from Westvaco in the form of pellets (2.1 mm extruded) and used as received except for regeneration.

Table 1. Measured isotherms and model correlations.

Adsorbate	P (torr)	T(K)	ARE_{SW}(%)	ARE_{VT}(%)
methane	4-4856	293-343	3.78	3.48
ethane	0.08-4948	293-363	6.28	29.91
propane	0.1-4934	293-363	2.94	19.04
n-butane	0.06-1483	293-363	5.17	13.79
n-pentane	0.07-100	293-363	4.67	6.14
n-hexane	0.06-100	293-363	6.97	7.43
n-heptane	0.15-59	293-393	13.44	13.58

Results and Discussion

The experimental adsorption isotherms were regressed using a step-wise (SW) regression method [3] and a virial-type (VT) [4] adsorption model. The average percent relative errors in pressure (ARE) from each model are shown in Table 1. The SW smoothing method was used here as an alternative for the conventional numerical differentiation of the equilibrium isotherm data according to the Clausius-Clapeyron equation. Simpler models such as Toth [5] and the heterogeneous Fowler-Guggenheim isotherm model with a uniform distribution of adsorption energies [2] were unable to represent all the systems reliably over the whole ranges of pressure.

Figure 1 shows ln$P$ (P in atm) as represented by the SW method versus the amount adsorbed, n (mole/kg), and the reciprocal temperature, $1/T$ (K^{-1}), for methane and n-heptane, the lightest and heaviest vapors studied. In this form of representation, ln$P$ can be easily visualized to have a linear dependence on $1/T$ at a fixed n. However, the SW statistical analysis of various forms of temperature dependencies of ln$P$ showed that the $1/T$ dependence can hardly provide any significant contribution to ln$P$, relative to higher orders of temperature dependencies, and that the $1/T$ dependence passes the t-test occasionally and with

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only low values. Moreover, this dependence becomes increasingly more complicated when more heavily adsorbed alkanes are considered.
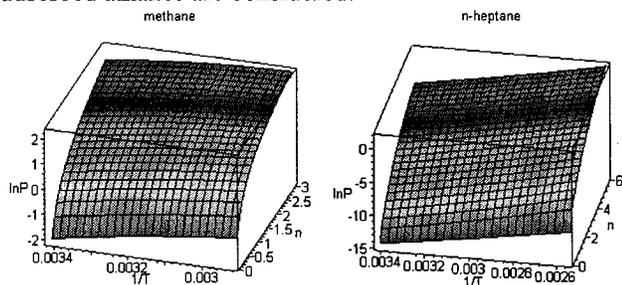

Figure 1. SW smoothing of $\ln P$ versus $1/T$ and n for methane and n-heptane on BAX activated carbon.

Figure 2 shows the resulting dependence of the isosteric heat of adsorption, q (kJ/mole), on n and T. Since the formulas obtained from the SW smoothing method depend solely on the adsorption equilibria of each specific system, it is less likely here to find any influence from the form of these formulas. In contrast, although the VT results gave the same magnitudes of isosteric heats of adsorption, they sometimes exhibited opposite temperature dependencies especially at extremely high loadings. But the VT model also misrepresented the adsorption equilibria at extremely high pressures, possibly due to the dense nature of the adsorbed vapor at these conditions, which disobeys the VT model which was originally designed for gas and low-to-moderate pressure, vapor phase equilibria. Overall, the temperature dependence of the isosteric heat of adsorption was relatively slight when considered over very narrow ranges of temperature and for relatively lightly adsorbed components.
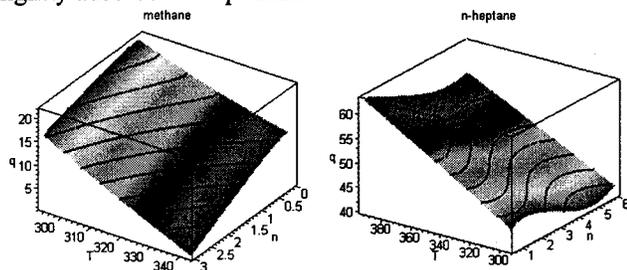

Figure 2. SW-predicted isosteric heats of adsorption of methane and n-heptane on BAX activated carbon.
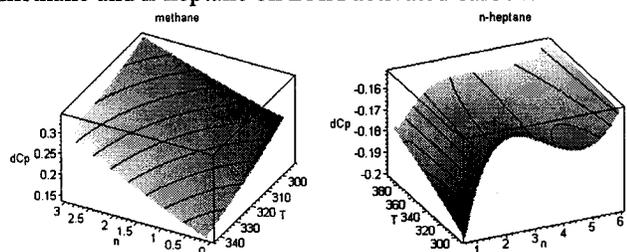

Figure 3. SW-predicted deviations between the differential adsorbed and molar gas phase heat capacities of methane and n-heptane on BAX activated carbon.

However, as a result of the relatively slight temperature dependencies of the isosteric heat of adsorption, deviations on the order of 0.05-0.5 kJ/mole.K resulted between the differential adsorbed and molar gas phase heat capacities as shown in Figure 3. Such deviations can constitute more than 20% of the gas phase heat capacity [2] which in turn can dramatically affect the accuracy of the simulation of adsorption processes [6]. So the slight temperature dependence of the isosteric heat of adsorption can be extremely important.

Conclusions

The temperature dependence of the isosteric heat of adsorption can easily be overlooked when plotting the adsorption equilibria according to the Clausius-Clapeyron equation. Therefore, the step-wise regression method was utilized here as a reliable alternative for the indirect estimation of the isosteric heat of adsorption from the statistically-smoothed dependence of the pressure logarithm on temperature at fixed loadings. This method of data smoothing had an advantage over the visual investigation of such dependencies by allowing different predictors to compete statistically on describing the objective variable. It also has an advantage over the different isotherm models when considered over extremely wide pressure ranges because its formulation depends totally on the specific systems studied. Direct experimental verification of the temperature dependence of the isosteric heat of adsorption and the deviation between the adsorbed and gas phase heat capacities is still strongly required.

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