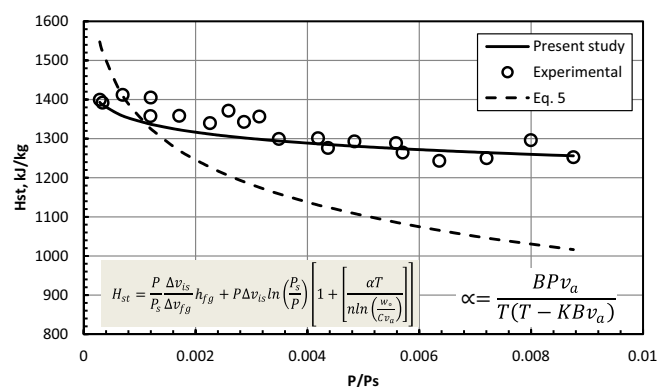Regular Article

Towards an accurate estimation of the isosteric heat of adsorption – A correlation with the potential theory

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GRAPHICAL ABSTRACT

Isosteric heat of adsorption of methane onto BPL activated carbon at 297 K.

$$H_{st} = \frac{P}{P_s}\frac{\Delta v_{is}}{\Delta v_{fg}}h_{fg} + P\Delta v_{is}ln\left(\frac{P_s}{P}\right)\left[1 + \left[\frac{\alpha T}{nln\left(\frac{w_s}{Cv_a}\right)}\right]\right] \qquad \propto = \frac{BPv_a}{T(T - KBv_a)}$$

ARTICLE INFO

ABSTRACT

Accurate estimation of the isosteric heat of adsorption is mandatory for a good modeling of adsorption processes. In this paper a thermodynamic formalism on adsorbed phase volume which is a function of adsorption pressure and temperature has been proposed for the precise estimation of the isosteric heat of adsorption. The estimated isosteric heat of adsorption using the new correlation has been compared with measured values of prudently selected several adsorbent-refrigerant pairs from open literature. Results showed that the proposed isosteric heat of adsorption correlation fits the experimentally measured values better than the Clausius-Clapeyron equation.

1. Introduction

Recently, adsorption characteristics of variety of newly developed adsorbent-adsorbate pairs have been reported for cooling applications [1–4]. These characteristics mainly contain uptake limits and isosteric heat of adsorption. In contrary of the adsorption uptake which is determined experimentally, the isosteric heat of adsorption is usually determined theoretically. Many equations have been proposed to predict the adsorption uptake and isosteric heat of adsorption such as Langmuir theory and adsorption potential theory [5].

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Validity of the adsorption potential theory which has been proposed by Dubinin-Polanyi has been tested frequently. Based on the Dubinin-Polanyi theory, many versions of adsorption uptake detecting equation have been presented in series trials to optimize the fitting of experimental data. The most recent presented version of the equations which predict the adsorption uptake based on the adsorption potential theory is the Dubinin-Astakhov (D-A) equation (Eq. (1)). It has been found in many experimental researches that it predicts the adsorption uptake well [6].

$$C = \frac{W_0}{v_a} exp\{-[\varepsilon]^n\} \tag{1}$$

where W_0 is the maximum volumetric adsorption capacity in cm³/g, v_a is the adsorbed phase specific volume in cm³/g, ε is the adsorption potential ($RTln(P_s/P)$) in kJ/kg and n is a fitting parameter.

For temperatures higher than critical temperature, Dubinin considered $v_a = 1/b$. Where, b is a constant of the Van Der Waals equation [7].

Assuming that the adsorbed phase can be treated as superheated liquid, Ozawa et al. [7] presented the below formula to estimate the v_a values.

$$v_a = v_b exp[\propto_s (T - T_b)] \tag{2}$$

where v_b is the normal boiling specific volume in cm³/g, α_s is the thermal expansion of superheated liquid and b refers to the normal boiling point.

Isosteric heat of adsorption has been derived based on the Clapeyron-Clausius equation and the D-A equation (Eq. (3)) [8].

$$H_{st_{CC}} = h_{fg} + E\left[ln\left(\frac{W_0}{Cv_a}\right)\right]^{\frac{1}{n}} + \frac{ET\alpha}{n}\left[ln\left(\frac{W_0}{Cv_a}\right)\right]^{\frac{1-n}{n}} \tag{3}$$

This equation has been widely used in the literature however it has been reported that it doesn't fit the measured isosteric heat of adsorption accurately [9]. Many trials have been carried out to improve this equation. Some efforts have been exerted to estimate the thermal expansion (α) where, Akkimaradi et al. [10] and Saha et al. [11] used the following expression for adsorption of HFC134a and HFC507a onto Maxsorb activated carbon.

$$\propto = \frac{ln\left(\frac{b}{v_a}\right)}{(T_c - T_b)} \tag{4}$$

where T_c is the critical temperature. Amankwah and Schwarz [12] proposed a constant value of α = 0.0025 K^{-1} for methane adsorption on four different specimens. In another study Saha et al. [13] used a formula of α = 1/T. Akkimaradi et al. [14] and Wang et al. [15] used α as a fitting parameter and optimized it from the least square fitting of the experimental data.

These trials cannot be generalized as for example using of v_b will be inapplicable for carbon dioxide which does not have a normal boiling point [16].

Srinivasan et al. [9,16] presented a new formula to estimate α based on the adsorbed phase specific volume (Eq. (5)).

$$\propto = v_a\left(B - \frac{\propto_g}{v_g}\right) \tag{5}$$

where v_g is the gas phase-specific volume, B is a fitting constant and α_g is the gas phase thermal expansion coefficient. This formula has been built based on the relation between v_a, v_g which has been assumed by Srinivasan et al. [16] (Eq. (6)).

$$v_a = \left(A - BT - \frac{1}{v_g}\right)^{-1} \tag{6}$$

where A is a constant. That was the first time considering pressure and temperature dependence of adsorbed phase specific volume.

This formula may be good to be used at high adsorption concentrations. At very low concentrations, it contradicts with the ideal gas law as the gas phase-specific volume becomes function only in temperature as below which is not true.

$$v_g = A - BT \tag{7}$$

Another point is at high temperatures the values of A-BT may become negative which means that the value of

$$\frac{1}{v_a} + \frac{1}{v_g} = A - BT \tag{8}$$

becomes negative as shown in Fig. 1. This value is a summation of densities, hence it is impossible to be a negative value. Fig. 1 also shows that at constant pressure the value of A-BT has no fixed trend for different adsorption pairs. Values of A and B which have been used in Fig. 1 have been taken from the literature.

From the previous discussion, it is clear that Eq. (6) can't be generalized. In this paper a new formula of the adsorbed phase specific volume has been presented and a new derivation for the isosteric heat of adsorption has been proofed.

2. Mathematical derivation

Assuming that the specific volume in adsorption phase is a linearly proportional with pressure and temperature this equation can be reached;

$$v_a = \left(A + B\frac{P}{T}\right)^{-1} \tag{9}$$

where

$$\propto = \frac{1}{v_a}\frac{\partial v_a}{\partial T} \tag{10}$$

$$\frac{\partial v_a}{\partial T} = -v_a^2\left(\frac{TB\frac{\partial P}{\partial T} - BP}{T^2}\right) \tag{11}$$

$$\frac{\partial v_a}{\partial T} = -v_a^2\frac{B}{T}\frac{\partial P}{\partial v_a}\frac{\partial v_a}{\partial T} + v_a^2\frac{BP}{T^2} \tag{12}$$

$$K = -v_a\frac{\partial P}{\partial v_a} \tag{13}$$

where K is the bulk modulus elasticity in kPa.
Hence;

$$\frac{\partial v_a}{\partial T} = \frac{v_a B}{T}K\frac{\partial v_a}{\partial T} + v_a^2\frac{BP}{T^2} \tag{14}$$

$$\propto = \frac{BPv_a}{T(T - KBv_a)} \tag{15}$$

$$\frac{1}{\propto} = \frac{T^2}{BPv_a} - \frac{TK}{P} = \left(-\frac{1}{v_a}\frac{\partial v_a}{\partial T}\bigg|_{P=c}\right)^{-1} - \frac{RK}{v_g} \tag{16}$$
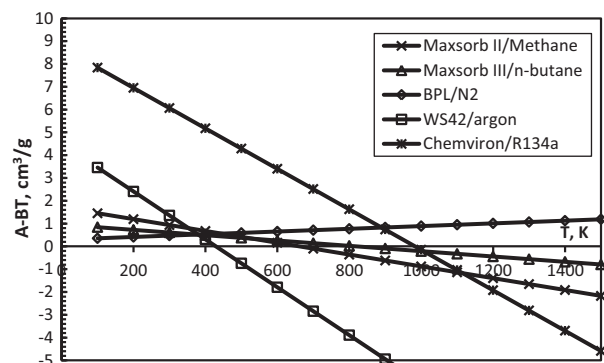

Fig. 1. Dependence of adsorbed phase density and gas phase density on temperature based on Eq. (6).