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Adsorption enthalpy of lead(II) and phenol on coals and activated carbon in the view of thermodynamic analysis and calorimetric measurements

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A B S T R A C T

Comparison among adsorption enthalpies of thermodynamic analysis and these of direct calorimetric measurements is reported for sorption of lead(II) and phenol on natural coals and activated carbon. Thermodynamic calculations came out from developments of equilibrium adsorption isotherms recorded at 303 K, 333 K and 353 K. Standard adsorption enthalpies ΔH^0 were calculated from temperature dependences of equilibrium constants of adsorption K_a, with values of K_a being evaluated directly from experimental data and from fitted courses of the Langmuir and Freundlich isotherms. In addition, dependences of isosteric enthalpy on surface coverage were evaluated. Values of the exothermic enthalpies (ranging from -6 kJ mol^{-1} to -50 kJ mol^{-1}) were obtained, however exclusive endothermic effect for lead(II) adsorption on a sample of natural coal (24 kJ mol^{-1}) was also ascertained. Direct calorimetric measurements using flow and immersion techniques then proved that all the studied adsorptions proceed with exothermic effects from -2 kJ mol^{-1} to -42 kJ mol^{-1}. It was found that experimental adsorption enthalpies correspond better to mean isosteric enthalpies in the interval 0–1 mol kg^{-1} of the surface coverages than to the standard adsorption enthalpies ΔH^0 of the thermodynamic calculations.

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1. Introduction

Adsorption from aqueous solutions is an important separation technique for water treatment, carbon based materials are being widely used as effective sorbents [1–5]. To gain complex information on the nature of the adsorption process, results from the thermodynamic analysis are of evident importance, with equilibrium constant (K_a), changes in Gibbs energy ΔG^o (J mol^{-1}), enthalpy ΔH^o (J mol^{-1}) and entropy ΔS^o (J mol^{-1} K^{-1}) of adsorption being evaluated as the basic parameters. Thermodynamic feasibility (ΔG^o) and the main driving forces (ΔH^o and ΔS^o) governing the adsorption process can thus be recognised. Mostly used way to perform thermodynamic analysis arises from courses of the adsorption isotherms measured at different temperatures [3,5]. Numerical values of the obtained parameters can be related to differently selected standard states [6,7] causing thus possible discrepancy in comparison among the published data [8]. In this respect, quantity of the adsorption enthalpy appears distinct since the values of ΔH^o are to be independent on the standard states reflecting rather ratio between values of K_a at different temperatures [6]. Of course, the values of adsorption enthalpy are directly available from the calorimetric experiments [9,10]; however, there is practically lack of simultaneous comparison of adsorption enthalpies from adsorption isotherms with these from the calorimetric measurements.

The paper refers such comparison for the adsorption of lead(II) ions and phenol on the samples of natural coals and activated carbon. It will be shown that the measured values of the adsorption enthalpy can considerably differ from these calculated ones, while the values of the experimental enthalpies are closer to the mean isosteric enthalpies rather than to the values of standard adsorption enthalpies ΔH^o.

2. Thermodynamic background

A crucial step in the thermodynamic calculations consists in determination of the equilibrium constant of adsorption K_a. Regarding the adsorption process in aqueous environment simply as an interaction between a solid sorbent (S) and an adsorptive (A), forming a solid adsorbate-sorbent adduct (AS), the corresponding equilibrium constant (K_a) can be written as

$$K_a = a_{AS}/(a_s \cdot a_A) \tag{1}$$

where a_s, a_A, a_{AS} are the activities at the equilibrium of the sorbent, the adsorptive and the adsorbate-sorbent adduct, respectively.

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Sorbent can be considered a solid in pure standard state; thus, its activity is equal to 1, hence $K_a = a_{AS}/a_A$. By rearranging the activities a_{AS}, a_A as functions of concentrations (c, mol kg^{-1}), activity coefficients (γ) and standard states (c^o, mol kg^{-1}), the Eq. (2) is obtained

$$K_a = \frac{(\gamma_{AS} \cdot c_{AS})/c_{AS}^0}{(\gamma_A \cdot c_A)/c_A^0} \qquad (2)$$

The choice of the standard states is arbitrary [6,7]; however, certain advantage offers selection of 1 mol kg^{-1} as a reference state both for solution of the adsorptive c_A^0 (presenting ideal solution with molality of 1 mol kg^{-1}) and the adsorbate-sorbent adduct c_{AS}^0 (presuming ideal behaviour of 1 mol of the adsorbate on 1 kg of the sorbent). This way, a dimensionless value of the equilibrium constant K_a is obtained.

In case of non-ionic adsorptives, activity coefficients γ_A can be approximated by 1. For ionic adsorptives, calculation of γ_A is available preferably using Debye-Hückel limiting law, though also values of γ_A are usually assumed to be 1 for ionic adsorptives [11–14]. Appropriate solution of the "non-ideality" of the adsorbate-sorbent adduct is seen in the extrapolation of the ratios $c_{AS}/(c_A \cdot \gamma_A)$ to zero surface coverage $c_{AS} \to 0$, when ideal behaviour of the sorbent-adsorbate adduct can be expected, making thus $\gamma_{AS} = 1$ [13–19]. Equilibrium constant of the adsorption can be then expressed as

$$K_a = \left(\frac{c_{AS}}{\gamma_A \cdot c_A}\right)_{c_{AS} \to 0} \qquad (3)$$

Eq. (3) is analogy with often used relation $K_a = q_e/c_e$, where q_e and c_e are common symbols for adsorption uptake and adsorptive concentration at equilibrium, respectively [12,20–29]. Such denotations for the adsorbed amount and concentration at equilibrium (both in the units mol kg^{-1}) are applied also further in this work. The ratio q_e/c_e is usually denoted as distribution coefficient K_d and generally leads to dimensional quantity of K_d.

Eq. (3) is also equivalent to the ratio between concentrations, $K_a = (c_0 - c_e)/c_e$, where c_0 and c_e are initial and equilibrium concentrations of the adsorptive solution, respectively [11,30]. Such simplified ratio between concentrations (as an equilibrium constant) is valid only if amount/mass both of adsorbent and adsorbate solution are invariable during the series of experiments. In this case, equilibrium constant is obviously dimensionless.

Knowing the values of the equilibrium constants K_a at different temperatures, enthalpy change ΔH^0 and change in entropy of adsorption ΔS^0 could be then evaluated from the slope and the intercept of the linearized dependence of the K_a on temperature in coordinates ln K_a versus $1/T$, respectively:

$$\ln K_a = -\frac{\Delta H^0}{RT} + \frac{\Delta S}{R} \qquad (4)$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}) and T is temperature (K). Formula (4) is known as the van't Hoff equation and it was derived provided that ΔH^0 as well as ΔS^0 are invariables within the temperature interval to be studied.

3. Experimental

3.1. Materials

Two samples of natural coals (denoted as A, H) and one sample of commercial activated carbon (AC) were investigated. The sample A was taken from the Upper Silesian Coal Basin and represents the type of oxidative altered bituminous coal [31]. The sample of low rank subbituminous coal (H) originates from the North Bohemian Coal District. The activated carbon (AC) was made from charcoal by chemical activation (Hrušovské chemické závody, Czech Republic).

Before the experiments, the samples were minimally twice washed in distilled water to remove the soluble impurities. The dried samples of a grain size between 0.06 mm and 0.25 mm were used for the measurements.

Description of the samples and further chemicals used is given in Table 1a.

3.2. Methods for characterization of the samples

The adsorption isotherms of carbon dioxide at 303 K (PCTPro HyEnergy, Setaram, France) were measured. Specific surface of the micropores S_{mi} was evaluated according to Medek [32].

The amphoteric character of the surface was estimated by Boehm acid/base neutralization titration [33], in which was assumed that NaOH neutralizes all acidic groups and HCl neutralizes all basic groups [34].

To estimate hydrophilicity/hydrophobicity of the surfaces, immersion enthalpies of the samples with water $\Delta_{im}H(H_2O)$ and benzene $\Delta_{im}H(C_6H_6)$ were determined at 303 K with the Setaram C80 calorimeter provided with a mixing vessel. A ratio $R^{W/B} = \Delta_{im}H(H_2O)/\Delta_{im}H(C_6H_6)$ was then evaluated as a parameter quantifying the surface hydrophilicity [35].

The basic analyses and properties of the samples are summarised in Table 1b.

3.3. Sorption investigations

Sorption of lead(II) ions (nitrate salt) and phenol from the aqueous solutions was studied at 303 K, 333 K and 353 K. The experiments were conducted in a batch mode. The flasks with suspensions (50 mL of adsorptive solution to 0.5 g of a sample) were capped and set on a thermostatic shaker and shaken for time period sufficient for equilibration. The lead(II) concentration of the filtered solutions was then determined by means of the ICP-AES (Perkin-Elmer Optima 3000 spectrometer) or AAS (Varian AA240 FS). Concentration of phenol was determined photometrically at maximum absorbance wavelength 500 nm after its reaction with 4-aminoantipyrine resulting in red-coloured condensate. The sorbed amounts q_e (mol kg^{-1}) were calculated from the difference between initial and equilibrium concentrations of the adsorptives. More experimental details are available in [36].

To describe the courses of the obtained sorption isotherms quantitatively, the Langmuir and Freundlich models [1–3] were applied.

The Langmuir model was verified in coordinates c_e/q_e vs. c_e resulting in the linear dependence:

$$\frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{q_m K_L} \qquad (5)$$

Table 1a
Description of samples and chemicals.

Chemical/ Sample Name	Source	Initial Purity	Purification Method
sample A	Upper Silesian Coal Basin, Czech Republic	–	washed with distilled H$_2$O (2x)
sample H	North Bohemian Coal District, Czech Republic	–	washed with distilled H$_2$O (2x)
sample AC	Hrušovské chemické závody, Czech Republic	–	washed with distilled H$_2$O (2x)
Pb(NO$_3$)$_2$	Penta	p.a.	none
phenol	Loba Feinchemie GmbH	p.a.	none
benzene	ONEX CHEMIE	p.a.	none
NaOH	Mach Chemikálie	p.a.	none
HCl	Mach Chemikálie	p.a.	none