

Adsorption heats of phenol on activated carbon using adapted method of immersion calorimetry

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Abstract Simple adaptation of the technique of immersion calorimetry enables determining both integral and differential adsorption heats as well as the course of the adsorption isotherm of phenol on activated carbon. The innovative aspect of the applied procedure consists in bringing the phenol aqueous solution to contact with the *suspension* of carbon with water. Thus, the “interfering” heat effect of carbon interaction with water is eliminated, and only the net adsorption heat of phenol is monitored. The value of $-52.5 \text{ kJ mol}^{-1}$ was ascertained as the molar differential adsorption heat at the low surface coverage (cca 0.2 mmol g^{-1}) of the sample of microporous carbon. As the adsorption process continues, for adsorption uptakes exceeding the value of about 1 mmol g^{-1} , molar differential adsorption heats appear to be established at a level of about $-20 \pm 5 \text{ kJ mol}^{-1}$.

Keywords Phenol · Carbon · Adsorption heat · Immersion calorimetry

Introduction

Adsorption of phenol on carbonaceous surfaces from aqueous solutions remains an important topic from both practical and research points of view [1, 2]. To understand the thermodynamic aspects of the phenol immobilization on the carbonaceous surface, adsorption heat is one of the fundamental parameters. To ascertain the values of the adsorption enthalpy, courses of adsorption isotherms

measured at different temperatures are often analysed, so offering information on (isosteric) adsorption heats [3–9]. Thus, both endothermic [3–7] and exothermic [7–9] heat effects of phenol adsorption on activated carbons were found with values varying from -42.4 [8] to 47.4 kJ mol^{-1} [4]. Direct calorimetric measurements of the phenol adsorption enthalpies are less frequent [2, 10–13]. In this respect, mainly flow adsorption and/or titration calorimetry are valuable techniques to gain reliable data [10, 12], giving evidently exothermic effects in all known cases. Also, “classical” immersion calorimetry provides valuable information on heat effects accompanying interactions taking part during immersion of the carbon sample in phenol aqueous solution [2, 11, 13]. However, measured immersion heats reflect both interactions of water (solvent) and phenol molecules with the surface and, thus, differentiation between these effects is necessary to obtain information on phenol adsorption heat only [2].

This article refers to simple adaptation of the immersion calorimetric technique to measure net adsorption heat of phenol on carbon from aqueous solution. In principle, such a procedure enables determining both integral and differential adsorption heats as well as the course of the adsorption isotherm of phenol on carbon.

Experimental

Activated carbon

A sample of commercial activated carbon (Hrušovské závody, Czech Republic) was studied. The sample is denoted as “HS3”, and its basic texture characteristics is given in Table 1. In total, the sample can be characterised as microporous activated carbon.

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Table 1 Basic characteristics of the studied sample

Sample	Carbon/ wt%, dry basis	$S^{\text{BET}}/\text{m}^2 \text{g}^{-1}$	$V^{\text{micro}}/\text{cm}^3 \text{g}^{-1}$	$H^{\text{im}}/\text{J g}^{-1}$
HS3	96.1	1150	0.485	36.8

S^{BET} surface area determined from adsorption of nitrogen at -196°C and evaluated according to BET theory

V^{micro} volume of micropores determined from adsorption of carbon dioxide at 25°C and evaluated according to Dubinin–Polanyi isotherm

H^{im} heat of immersion of the dried sample in water at 30°C (average value of 12 measurements)

Calorimetric procedure

For the experiments, a Setaram C80 calorimeter (France) equipped with mixing cell was used. Measurements were performed at a temperature of 303 K and pressure about 100 kPa.

The innovative aspect of the applied procedure consists in bringing the phenol aqueous solution into contact with the *suspension* of carbon with water. Thus, the “interfering” heat effect of carbon interaction with water (of about 36 J g^{-1} , see Table 1) is eliminated, and only the net adsorption heat of phenol is monitored. For the measurements, suspension of 0.15 g of the sample (grain size less than 0.06 mm) with 0.8 mL of water was inserted into the lower part of the calorimetric cell, and 3.0 mL of phenol aqueous solution was placed in the upper part of the cell, over the membrane. Phenol concentrations from 10 to 400 mmol l^{-1} were used to cover a wide range of possible adsorption uptakes of the phenol on carbon surface.

In principle, such a procedure is very similar to the technique of titration calorimetry as described recently for adsorption of phenol on zeolites [14]. However, the proposed variation of the immersion technique offers the possibility to determine phenol concentration in the mixture immediately after the calorimetric measurement and, consequently, the value of the adsorbed amount of phenol for each measured heat can be determined. This advantage was employed in the study, the phenol concentration being determined using liquid chromatograph Agilent 1200 (USA) equipped with DAD detector.

Finally, it is worth mentioning that a series of blank experiments were performed to evaluate heat of membrane perforation (about -80 mJ) and/or heat of mixing (about -50 mJ) occurring during calorimetric measurement and possibly interfering with the measured heats.

Results and discussion

Perforation of the membrane dividing the calorimetric cell and mixing the suspension initiated the phenol adsorption

process accompanied by an evident exothermic peak. The baseline of the calorimetric signal was restored within about 50 min. However, subsequent mixing of the suspension resulted in another exothermic peak representing about 12% of the former. Obviously, the stage of fast phenol adsorption changed into a slow diffusion step with a much lower heat evolution rate that could be “hidden” in the baseline. However, repeated mixing of the suspension restored the stage of fast adsorption inside the mixture. Hence, mixing the suspension was repeated until the resulting heat effect was comparable with the level of the mixing blank. In practice, it was necessary to perform four additional mixings, and, afterwards, it was possible to assume equilibration of the system. In total, equilibration took about 4 h, which is quite comparable to times reported by other authors [4, 6, 8]. The net value of the adsorption heat of one calorimetric test was then obtained as a sum of the subsequent heat effects.

Figure 1 displays the integral adsorption heats Q^{int} (J g^{-1}) as a dependence of the phenol adsorption uptakes n_a (mmol g^{-1}). Adsorbed amount n_a was determined from the initial and the equilibrium concentrations of phenol in the calorimetric cell.

Irrespective of the scatter of the plotted data (coefficient of variability is estimated to be about 3%_{rel}), the dependence is obviously of non-linear character, giving first a sharp rise in the adsorption heats, followed by a rather gradual and monotonous increase in the Q^{int} values. This finding is different from the convincing linearity ascertained by MacDonald and Evans [10]. However, their results were obtained for a narrow range of surface coverage varying between 0.01 and 0.1 mmol g^{-1} while here reported heats cover a wide range from 0.2 to 3.7 mmol g^{-1} . To compare the obtained integral adsorption heats with the other published results are not so simple as the data in the literature are not usually related to known adsorption uptakes. Thus, values from -10 [2] to -76 J g^{-1} [12] can be found in the literature, all these

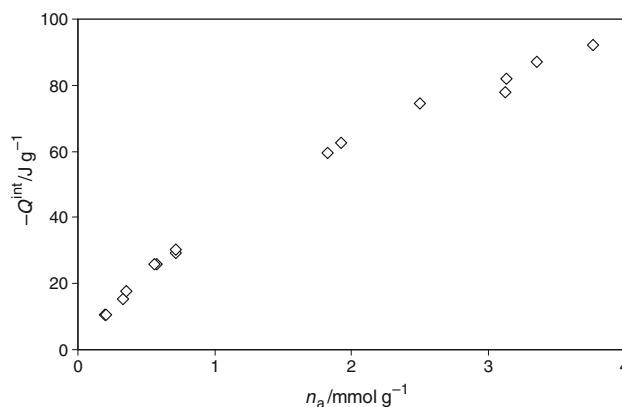


Fig. 1 Integral adsorption heat of the phenol Q^{int} on activated carbon HS3 as a function of phenol adsorption uptake n_a

values being quite reasonable also for the HS3 sample studied here; however, at different values of the phenol adsorption uptake.

Derivation of the integral heat curve (as displayed in Fig. 1) enables obtaining the values of the differential molar adsorption heat Q_m^{dif} (kJ mol^{-1}) at given adsorption uptakes. Figure 2 thus shows the evolution of the determined values of Q_m^{dif} as a function of the adsorbed amount of phenol.

Marked initial decrease in the values of Q_m^{dif} is evident here, proving strong heterogeneity of the adsorption sites on the sample surface. The highest value of $Q_m^{\text{dif}} = -52.5 \text{ kJ mol}^{-1}$ ascertained for the lowest surface coverage is well comparable with the value of $-54.5 \text{ kJ mol}^{-1}$ reported by MacDonald and Evans [10]. As the adsorption process continues, the drop in the value of Q_m^{dif} runs out, and differential molar adsorption heats appear to be established at a level of about $-20 \pm 5 \text{ kJ mol}^{-1}$. The “stabilization” of the Q_m^{dif} values can be observed for adsorption uptakes exceeding the level of about 1 mmol g^{-1} .

Finally, Fig. 3 demonstrates the shape of the adsorption isotherm of phenol on sample HS3 as determined using the analyses of the phenol concentrations at suspensions in the calorimetric cell before and after the calorimetric measurements.

The ascertained adsorption isotherm is of typical Langmuir (L) shape. Tight consistency of the isotherm with the Langmuir model was confirmed by regression coefficient of R^2 close to 1 ($R^2 = 0.995$, see inset in Fig. 3). Simultaneously, monolayer adsorption capacity n_m of the studied carbon to phenol was calculated from the slope of the linearized Langmuir plot giving the value of $n_m = 3.8 \text{ mmol g}^{-1}$. In this respect, it is worth pointing out that such a value of n_m is well comparable with the monolayer surface coverage 4.1 mmol g^{-1} found earlier in

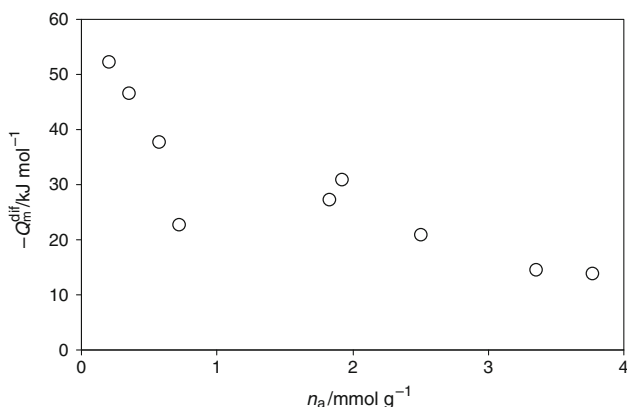


Fig. 2 Differential molar heat of phenol adsorption Q_m^{dif} on activated carbon HS3 as a function of amount of phenol adsorbed n_a

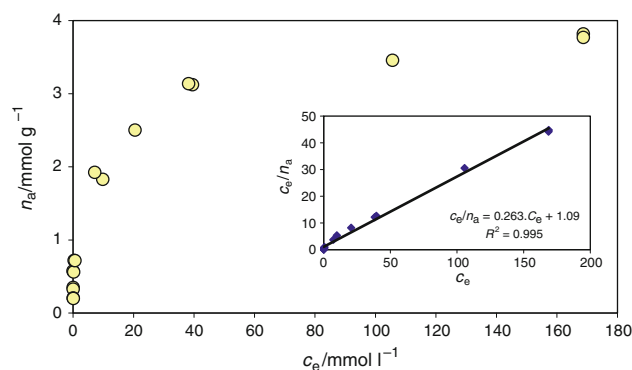


Fig. 3 Adsorption isotherm of the phenol on activated carbon HS3; $30 \text{ }^\circ\text{C}$, $\text{pH} \sim 5$, c_e is the equilibrium concentration of phenol; *inset* is the linearized Langmuir plot

adsorption investigations of the sample using the “classical” batch adsorption experiments [15].

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