

INDISPENSABILITY OF THE USE OF CALORIMETRIC MEASUREMENTS FOR THE DESCRIPTION OF ADSORPTION PROCESSES IN MICROPOROUS SYSTEMS

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Abstract

The role of calorimetry in adsorption is shortly reviewed. The differences between calorimetric adsorption heats and those calculated from Clausius-Clapeyron equation for the systems ethanol-activated carbons are presented. Obtained results, together with the results presented previously for other adsorbates, confirm that calorimetry is indispensable for a real thermodynamical description of the adsorption process in this type of system.

Keywords: activated carbon, adsorption, adsorption calorimetry

Introduction

Calorimetry plays an important role in surface chemistry [1] especially in adsorption [2, 3] and catalysis [4, 5]. It is applied for determination of adsorption mechanisms of vapours (or gases) [6, 7] and their mixtures [8] on homogeneous surfaces (for example on carbon blacks) and for determination of acid-base surface properties [9-11] or energy distribution functions [12] of heterogeneous materials. This method can be used also for determination of surface areas of different solids [13] or for verification of some methods for this area estimation [14]. Application of adsorption calorimetry alone or with another methods (for example IR spectroscopy [15] or neutron diffraction [16]) makes it possible to determine the molecular motions of adsorbates in zeolites [17] or adsorption mechanism on microporous activated carbons [18-20]. The adsorption mechanism can be verified by calculation of the integral entropy and heat capacity of an adsorbate [19]. The adsorption heat measurements by immersion technique plays an important role in characterization of carbon blacks [21] and microporous activated carbons [22-25]. Adsorption heat measurements and application of different theories give valuable information concern-

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ing the state of metal cations adsorbed in carbon pores [26]. In this paper we present the comparison of calorimetric adsorption heat with so called 'isosteric' adsorption heat. The latter was calculated from temperature dependence of the adsorption isotherms for the systems: ethanol – microporous activated carbons.

Experimental

The adsorption of ethanol on microporous activated carbons obtained from poly(furfuryl) alcohol was investigated. The initial carbon (A) with negligibly small concentration of oxygen functionalities was oxidized using nitric acid carbon (B). The detailed procedure of carbon preparation and carbon characteristics were given previously [19, 20]. Differential heats of adsorption (Figs 1 and 2) were determined at: 308, 328, 348 and 363 K, with the accuracy of $\pm 1.5\%$ using a Tian-Calve microcalorimeter. Adsorption isotherms (Figs 3 and 4) were measured volumetrically using the type of apparatus described by Kiselev [27] containing microburettes with liquid adsorbate and greaseless vacuum valves.

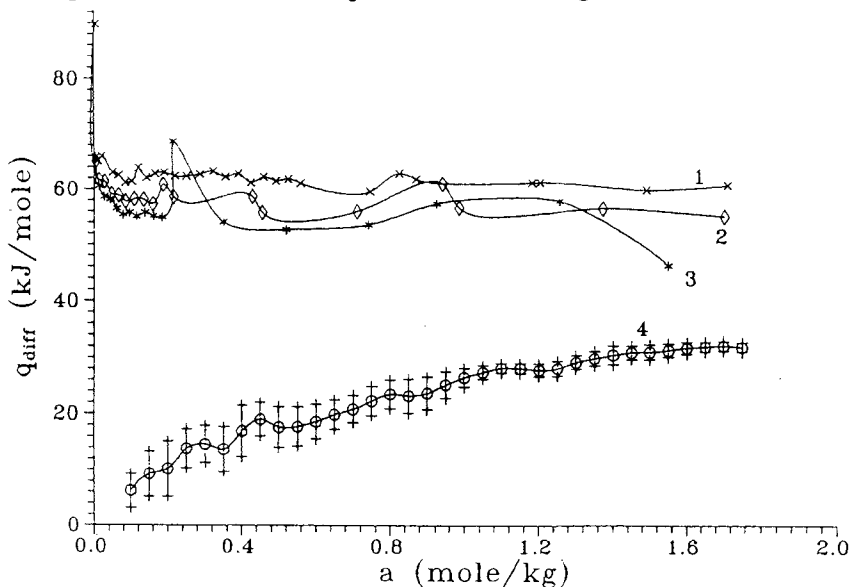


Fig. 1 Calorimetric differential heat of ethanol adsorption on A type carbon at: 308 K (1), 328 K (2) and 348 K (3) and the isosteric adsorption heat (4) reduced by the RT term. Centered symbols height denote the differential heat error. The error of isosteric heat is marked by error bars

Results and discussion

The isosteric adsorption heats were calculated according to Clausius-Clapeyron equation [29]. We assumed the linearity of adsorption isosteres.

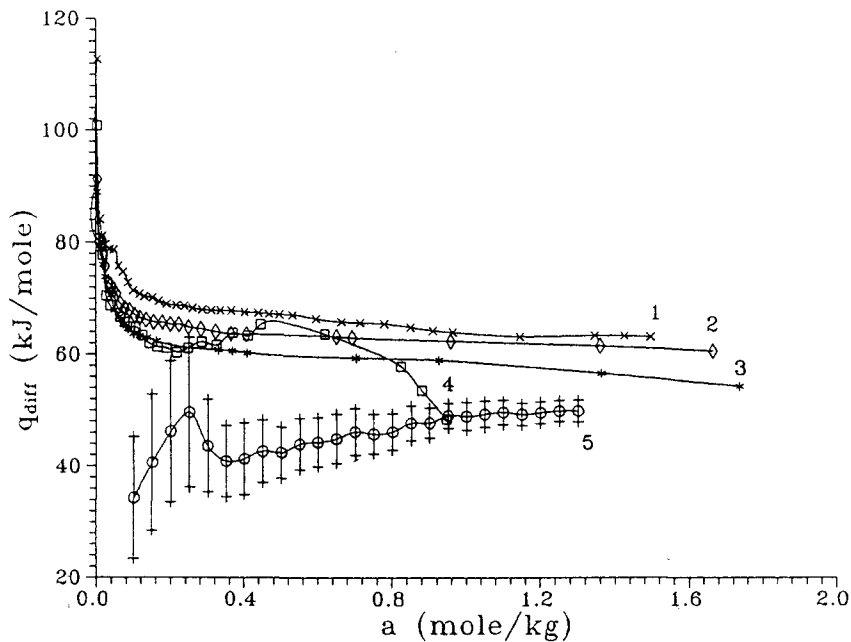


Fig. 2 Calorimetric differential heat of ethanol adsorption on B type carbon at: 308 K (1), 328 K (2), 348 K (3) and 363 K (4) and the isosteric adsorption heat (5) reduced by the RT term

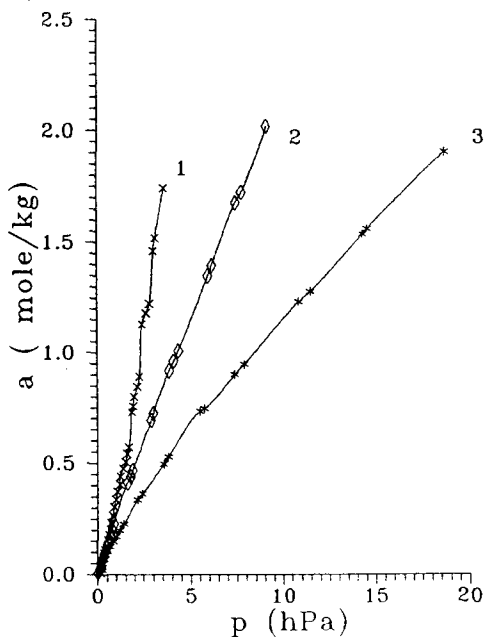


Fig. 3 Adsorption isotherms of ethanol on A type carbon at: 308 K (1), 328 K (2) and 348 K (3)

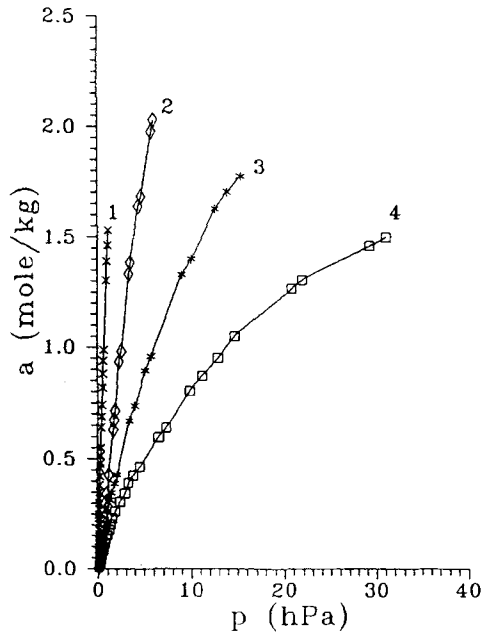


Fig. 4 Adsorption isotherms of ethanol on B type carbon at: 308 K (1), 328 K (2), 348 K (3) and 363 K (4)

These heats are presented on Figs 1 and 2 and compared with calorimetric heats. The comparison of calorimetric ethanol adsorption heats with those obtained from adsorption isosteres shows that the isosteric adsorption heats differ from the calorimetric ones and the observed differences are similar to those reported for other adsorbates [28, 29]. They occur for adsorption heats on both carbon surfaces.

The probable reasons of obtained differences were given previously [28, 29]. It was shown that the molecular sieve effect, occurring in this type of adsorption systems, causes an irreversible adsorption in carbon micropores. This effect is probably connected with the structural changes of the adsorbent [30] and with the low pressure hysteresis. The irreversibility of adsorption in micropores was often reported, and we think that this effect is mostly responsible for the uselessness of adsorption heat calculated from isosteres.

The general conclusion of this paper is that the adsorption isotherms measurements give no evidence on the structure of the adsorbed phase. Hence, additional methods, which can be applied 'in situ' to physisorption measurements, are necessary for the structural elucidation of the adsorbate. The results of this paper and those presented previously show that calorimetry is irrevocable in microporous systems for a real thermodynamical description of the adsorption process.

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Zusammenfassung — Es wird ein kurzer Überblick über die Rolle der Kalorimetrie bei der Adsorption gegeben. Die Differenzen zwischen den kalorimetrischen Adsorptionswärmern und den anhand der Clausius-Clapeyron-Gleichung berechneten Werte für das System Ethanol/Aktivkohle werden dargelegt. Zusammen mit unlängst veröffentlichten Ergebnissen für andere Adsorbate bestätigen die erhaltenen Ergebnisse, daß die Kalorimetrie für eine reelle thermodynamische Beschreibung des Adsorptionsprozesses in diesem Typ von Systemen unentbehrlich ist.