

INTEGRAL MOLAR ADSORPTION HEAT IN THE SYSTEM ACTIVATED CARBON-BENZENE AT 20°C

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In a calorimeter the heats of immersion of the activated carbon SSHR were measured in benzene at 20°C. The values of the heats of immersion for the pure surface of the evacuated sample as well as for the surface partially covered with benzene, which was adsorbed from gas phase, were compared with the values of integral adsorption heats. The integral adsorption heats were obtained by integration of isosteric adsorption heats, which were calculated from the adsorption isotherm of benzene. The isotherms were measured on the same sample of activated carbon at 20 and 25.8°C.

In the study of physical adsorption of gases on solid materials the integral adsorption heat is one of the principal parameters that are necessary for the evaluation of the state of adsorbate in an adsorbed layer. As the equilibrium for one point of isotherm is reached in 1–6 hours, the direct measurement of adsorption heats is tiresome. Their calculation from isothermal equilibrium data is subjected to inaccuracy due to assumptions used in the derivation of thermodynamical models of adsorption systems and to experimental difficulties in the measurement of the initial part of isotherm. That is why the values of calculated integral adsorption heats are subjected to errors which make troublesome any quantitative discussion of the properties of an adsorbed layer.

In this paper the method of the correlation of calculated integral adsorption heats is suggested. It consists in the comparison of the calculated integral adsorption heats with the measured immersing heats for the same system. However the region of the adsorbed amounts has to be close to the maximal adsorption (*i.e.* for $a/a_m = 0.8-1$).

THEORETICAL

According to the definition the integral molar adsorption heat $(u_A)_a$ is the heat that is exchanged with environment if $1/a$ mol of an adsorbate are adsorbed on 1 g of evacuated adsorbent. Integral molar adsorption heat $(u_A)_a$ can be calculated by relations^{1,2}

$$(u_A)_a = 1/a \int_0^a q_{st}(a) \cdot da + RT, \quad (1)$$

$$q_{st} = -RT^2(\partial \ln p/\partial T)_a, \quad (2)$$

where q_{st} is the isosteric adsorption heat, R is the gas constant, T is the temperature in K, p is the equilibrium pressure of an adsorbate in gas phase at the temperature T and for the adsorbed amount a .

The isosteric adsorption heat q_{st} was calculated from the integrated form of equation (2) under the assumption of independence of q_{st} on temperature. The validity of this assumption is confirmed for a narrow temperature interval only.

If the equilibrium pressure of an adsorbate in gas phase equals to the pressure of its saturated vapours at the temperature of the isotherm then the adsorbed amount reaches its maximal value a_m . The integral molar adsorption heat in this case also reaches the maximal value $(u_A)_m$. From thermodynamical conditions of equilibrium it follows: Integral molar adsorption heat for the maximal adsorption $(u_A)_m$ equals to the heat $(h_{im})_e$ related to one mol of adsorbate which is exchanged with the environment when the evacuated adsorbent is immersed in liquid adsorbate plus molar condensation enthalpy. In any immersing process no volume work is done. Hence it can be written:

$$(u_A)_m = (h_{im})_e + h_{cond} = 1/a_m \int_0^{a_m} q_{st}(a) \cdot da + RT, \quad (3)$$

where $(h_{im})_e$ is the immersing heat of the evacuated sample of adsorbent related to 1 mol of adsorbate. In the calculation it was assumed that the amount which was adsorbed on adsorbent in the immersing process equals to the maximal amount adsorbed in the adsorption from gas phase; h_{cond} is the molar condensation heat of adsorbate; $(u_A)_m$ is the integral molar adsorption heat at maximal adsorption.

The amount of heat $(a_m - a) \cdot (h_{im})_a$ is released on immersing of 1 g of the adsorbent on which a mol of adsorbate has been preadsorbed. On the basis of the considerations about the immersing process the following relations can be written:

$$(h_{im})_a = (a_m - a)^{-1} \int_a^{a_m} q_{st}(a) \cdot da + RT - h_{cond} \quad (4)$$

and

$$(h_{im})_e - (a_m - a) \cdot a_m^{-1} \cdot (h_{im})_a = a_m^{-1} \int_0^a q_{st}(a) \cdot da + aRT/a_m - ah_{cond}/a_m. \quad (5)$$

Relation (5) enables the comparison of the experimental values of heats of immersion related to 1 mol of adsorbate with the values calculated from isothermal data.

EXPERIMENTAL

As in the previous works³ the samples of activated carbon Supersorbon Hrušov of the size 0.4 to 0.6 mm were used. Benzene purified by multiple crystallization and by rectification⁴ was used as an adsorbate. Three physical constants were measured and compared with the tabulated data⁵

of pure benzene: b.p. 80.06°C (lit. 80.10°C); n_{20}^D 1.5010 (lit. 1.5001); density d^{10} 0.8790 g/ml (lit. 0.8790).

Gravimetric adsorption apparatus, which is schematically shown in Fig. 1, was used in the measurements of adsorption isotherms. Its main part was an adsorption tube with quartz spiral balances. Its sensitivity was 4 mg/mm. A quartz hook and a nickel basket with adsorbent A were fixed on the spiral balances. The adsorbent was kept at the particular temperature by Hoepler thermostat. The adsorption tube was connected with U-manometer and with two McLeod manometers with different compression volumes which had their ranges of measured pressures partially overlapped. The elongation of the spiral and the heights of the mercury levels were measured by cathetometer with the precision of 0.02 mm. The adsorbate was added from the reservoir R using the mercury valve. For the evacuation of the apparatus the vacuum line with rotatory oil and mercury diffusion pumps was used. The whole apparatus was placed in the air thermostat the temperature of which was by 10°C higher than that of adsorption tube with the spiral balances. To control the mercury level in the apparatus the external pressure and the vacuum line were utilized. All measurements were carried out by usual means. The time necessary for equilibrium to be reached was close to 3 hours. For the measurement of the immersing effect an immersing calorimeter and an adsorption apparatus were built. The adsorption apparatus (Fig. 2) was used for the formation of the preadsorbed layer on adsorbent prior to immersing. This apparatus consist of four ampoules of the known weights with the samples of activated carbon, U manometer and the reservoir of liquid adsorbate. Into each of the four ampoules 1.0–1.5 g of activated carbon was weighted in air. The ampoules were connected by ground joints with the apparatus and the samples of activated carbon were evacuated for about five hours at 350°C up to the vacuum of 10^{-5} Torr. Then one of the ampoules was sealed off the adsorption apparatus. The remaining three ones were thermostatted to 20°C . Then the reservoir with liquid adsorbate was opened and adsorption equilibrium was let to establish for c. three hours. Afterwards the ampoules were sealed off.

From the weight of the empty ampoules, the weight of activated carbon in air and from the weight of the evacuated ampoule with the sample of activated carbon the weight of pure evacuated

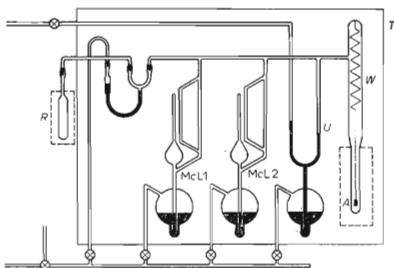


FIG. 1

Adsorption Apparatus with Spiral Balances

W Quartz spiral balances, A basket with adsorbent, McL1 and McL2 McLeod vacuumeters, R reservoir of adsorbate, T air thermostat.

activated carbon in the other ampoules could be calculated. From the weight of the ampoules with preadsorbed benzene on activated carbon and from the weight of pure activated carbon, which was calculated according to the above mentioned procedure, the total amount of adsorbed benzene could be calculated. The immersing calorimeter is schematically shown in Fig. 3. Temperature was measured by a mercury calorimetric thermometer with the 0.01°C division. The temperature reading was carried out by means of an optical device which avoided any paralaxa error.

The thermal capacity of the calorimeter was determined by a compensation circuit. It was found that the effect of the destruction of the sample tube is negligible and smaller than 0.2 J.

All measurements were carried out in the following way: After fixing the sample tube into the destruction device the calorimeter was put together and connected. The temperature course of the calorimeter was stabilized in the region of 20°C in two hours. The sample tube was broken and temperature was again stabilized. Then the heat capacity of the calorimeter was measured. From the both curves (*i.e.* from the curves of the time dependencies of temperature for the immersing process and for the determination of the thermal capacity of the calorimeter) the values of heat of immersion were determined. The immersing heats were measured with the precision of 1% in this calorimeter.

The found values of the heats of immersion are given in Table I. The values of the immersing heats of the evacuated sample of activated carbon are the means of 12 measurements, the values for the samples with preadsorbed benzene are the means of three measurements.

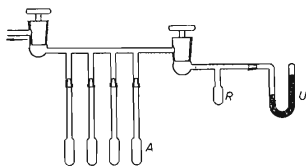


FIG. 2

Apparatus for the Preparation of Samples for Immersing Calorimeter

A Ampoules for the samples of activated carbon, R reservoir of adsorbate, U mercury manometer.

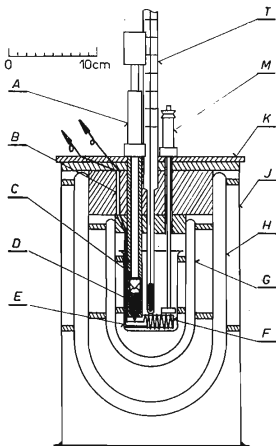


FIG. 3

Calorimeter for Measuring Heats of Immersion

A Device for the destruction of sample tube, B expanded polystyrene, C rod of the destruction device with spikes, D tube with the sample of adsorbent, E reservoir for liquid adsorbate, F heating of calibration circuit, G H Dewar flask, J metallic jacket of calorimeter, K PVC lid, M mixer, T calorimetric thermometer.

RESULTS AND DISCUSSION

The adsorption isotherms of benzene on activated carbon are presented in Fig. 4.

The calculation of integral molar adsorption heat is subjected to an uncertainty which is caused by difficulties in the correct measurement of adsorption isotherm in the region of equilibrium pressures 10^{-6} – 10^{-2} Torr. This uncertainty makes troublesome the quantitative evaluation of the properties of an adsorbed layer. In the next part we shall try to show that this property can be overcome by comparison of calculated integral molar adsorption heats with measured immersing heats. We start from equation (5) which has to be transformed into the following form:

$$(h_{im})_e - (a_m - a) a_m^{-1} \cdot (h_{im})_a =$$

$$= a_m^{-1} \int_0^{a_0} q_{st} \cdot da + a_m^{-1} \int_{a_0}^a q_{st} \cdot da + aRT/a_m - ah_{cond}/a_m, \quad (6a)$$

$$= a_0 I(a_0)/a_m + a I(a)/a_m + aRT/a_m - ah_{cond}/a_m. \quad (6b)$$

All terms of equation (6b) are directly measurable or they can be calculated with adequate precision from the experimental data except for the term $I(a_0)$. However, this value can be explicitly expressed from of relation (6b).

$$I(a_0) = a_0^{-1} \{ a_m (h_{im})_e - (a_m - a) (h_{im})_a - a(h_{cond} - RT) - aI(a) \}. \quad (7)$$

TABLE I

The Values of Immersing Heats, Integrals $I(a)$ and $I(a_0)$, and Deviations $\Delta I(a_0)$ from the Mean Value $I(a_0)$ in the Dependence on the Fraction of Surface Covered

a^a mmol g ⁻¹	$(h_{im})_a$ J mmol ⁻¹	$I(a)^b$ J mmol ⁻¹	$I(a_0)^c$ J mmol ⁻¹	$\Delta I(a_0)$ %
0	-18.7 = $(h_{im})_e$	—	—	—
5.39	-11.8	-5.4	-60.5	0.7
6.02	-12.8	-9.1	-61.4	2.2
6.27	-26.4	-10.7	-59.6	-0.8
6.38	-33.7	-11.4	-59.4	-1.2
6.44	-36.6	-11.6	-59.5	-1.0
6.84	—	—	—	—

^a The amount of benzene adsorbed from gas phase; ^b $I(a) = a^{-1} \int_{4.56}^a q_{st} da$; ^c mean value of $I(a_0) = 60.1$.

If the values of $I(a_0)$ from the last relation are the same for different preadsorbed amounts then the possibility can be assumed of the correlation of integral molar adsorption heats by means of heats of immersion. The obtained results would be subjected only to the errors of the scattering of the experimental data and to the inadequacy of the generally used thermodynamical models of the adsorption system. The errors of the scattering of the data can be evaluated from the variance of data.

The value of $I(a_0)$ was calculated in the dependence on the amount of preadsorbed benzene. The calculated values of $I(a_0)$ together with the experimental values of the immersing heats and the integral molar adsorption heats that are necessary for the calculation are given in Table I. The values of adsorption were expressed in millimol of benzene on 1 g of activated carbon. The heats of immersion as well as the integral adsorption heats were related also to one millimol of benzene. In the calculation the volume of 4.56 mmol g^{-1} was chosen for a_0 because the repeated measurements of adsorption isotherms in the region of low pressures showed that the isotherms are well reproducible only if the adsorbed amount is higher than this value. The condensation heat of benzene $h_{\text{cond}} = -33.693 \text{ J mmol}^{-1}$ at 20°C .

Table I shows that $I(a_0)$ equals to 60.1 mmol and that in the studied region of adsorption ($5.39 - 6.84 \text{ mmol g}^{-1}$) is constant within the 2.2% deviation from the mean value. This fact shows that the correlation of integral adsorption heats by means of immersing heats is possible. To be able to evaluate the $I(a_0)$ value the immersing heat of the evacuated sample of adsorbent and one sample of adsorbent with preadsorbed adsorbate must be measured.

The results proved that the presented method of the correlation can be used with sufficient accuracy in such a region of isotherm in which along with a significant change of pressure the adsorbed amount is hardly changed. From the point of view of the comparison of immersing heats and integral adsorption heats the mentioned region of adsorption isotherm is important with respect to the fulfillment of the assumption of inert adsorbent.

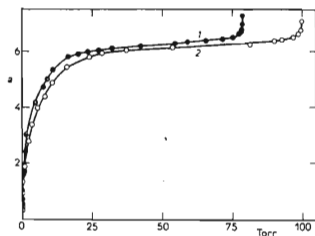


FIG. 4

Adsorption Isotherm of Benzene on the SSHR
Activated Carbon

1 20.0; 2 25.8°C; a in mmol/g.

If this assumption is not fulfilled in the investigated system then equation (3) is not generally valid due to possibility of deviations from inert behaviour that affects only the values of heats of immersion and does not affect the values of integral adsorption heat. The approximative constancy of the $I(a_0)$ value proves that, in the chosen region of isotherm, the assumption of inert behaviour of the adsorbent is satisfactorily fulfilled. If there are some deviations from the inert behaviour of adsorbent in the initial part of adsorption isotherm then their effect is included in the value of $I(a_0)$.

The presented method enables to correlate the course of the dependences of both compared heats on the adsorbed amount even for a non inert adsorbent. However, unlike to the case of inert adsorbent, there is not possible any quantitative comparison of the values of these two quantities.

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