Adsorption equilibria of water vapour on active carbon*

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On the basis of analysis of the adsorption and desorption equilibria of water vapour on active carbon the existence of an undercooled adsorbed phase up to the temperature of −30°C was found. The limit of stability of adsorbed water vapour was determined by the application of the thermodynamic condition and was compared with the limit of stability of liquid phase. The experimentally determined limit of stability of the adsorbed phase did not comply with the calculated limit of stability of the liquid phase, nevertheless it showed an analogous temperature dependence.

На основе анализа адсорбционного и десорбционного равновесия паров воды на активированном угле было найдено существование переохлажденной адсорбированной фазы при температуре —30°C. Предел устойчивости адсорбированных паров воды был определен применением термодинамических условий и сравнивался с пределом устойчивости жидкой фазы. Экспериментально определенный предел устойчивости адсорбированной фазы не согласуется с рассчитанным пределом устойчивости жидкой фазы, хотя температурна зависимость протекает аналогично.

In the study of adsorption equilibria of water vapour on active carbon a specific behaviour which is characteristic for all types of this adsorbent and entirely different from other adsorbates may be observed. The adsorption properties of water vapour are most evident on the isotherms. These dependences have a typically S-shaped form with a pronounced hysteresis loop; a steep decrease of the adsorbed amount is obvious at 20°C in the close vicinity of the relative pressure 0.5. The given property of the desorption branches of the hysteresis loops of water vapour isotherms does not depend on the porous structure of active carbon and was found also with some other adsorbents [1]. This property has been discussed in detail before [2], not only for the case of desorption equilibria of the system water—active carbon but also for other systems. It was proved that the characteristic pressure, corresponding to the junction of both branches of the hysteresis loop, generally does not depend on the nature of the adsorbent and is a property of the adsorbate only. This was explained by the fact that the capillary-condensed phase in the pores under the negative pressure attains the limit of its stability; behind this limit its existence is no more possible.

The above explanation has been verified for a series of systems [3]. There have not yet been, however, any systems where water was the adsorbate. For this reason, adsorption and especially desorption equilibria of water vapour on active carbon were studied in this paper. The studies were made in the temperature interval including temperatures below the triple point of water.

Experimental

The temperature dependence of the adsorption equilibria of water vapour was investigated on active carbon HS-4, produced by Moravské chemické závody (Moravian Chemical Works) in Ostrava — Hrušov by the zinc dichloride activation of the raw wood at 600—650°C. This adsorbent contains considerable amount of salt which influences the adsorption equilibria of water vapour [4]. Therefore, before measurements the adsorbent has been extracted by water in a Soxhlet apparatus until all soluble substances were completely removed.

The temperature dependence of the adsorption equilibria was measured in a volume apparatus with a microburette [5]. The sample of active carbon was first evacuated for 20 hrs at 350°C until a vacuum of 10^{-6} torr was reached. Known amounts of water vapour were subsequently added to the evacuated sample; after each addition, the dependence of the equilibrium pressure of adsorbate vapours on the adsorbent temperature was measured. Taking into account that the dead space volume in the apparatus was very small, almost all water was present in the adsorbed phase and the dependences obtained approached adsorption isosteres. Since the dead space volume was determined, the deviations from isosteric conditions were estimated in all calculations.

Almost all dependences were measured in the region of adsorption hysteresis. However, they were reversible, *i.e.* the points obtained in both directions of temperature changes were on the same line. Adsorption and desorption scanning of the hysteresis loop caused by the deviation from the isosteric conditions took place only in a minimum range and the errors arisen were within the experimental error. We have chosen such a dosing procedure that the cumulation of the above errors could be avoided. After the measurement of each temperature dependence of the equilibrium pressure the sample was evacuated for 8 hrs at 100°C and a new dose of vapour was added at 20°C to the clean adsorbent. During the process of adding the appropriate direction of pressure changes was maintained (*e.g.* in the desorption part of the hysteresis loop the adsorption to the relative pressure equal to 1 was first performed, then the desorption to the requested point followed, and only then the dependence of the equilibrium pressure on temperature was measured).

Results

On the basis of the obtained results of temperature dependence of the equilibrium pressure of water vapour measured in the temperature range $-30-+30°C$ and the relative pressure range $0.05-1.00$, adsorption and desorption isotherms and isosteres were calculated. In the coordinates $\log p$ *vs.* $1/T$ all isosteres were linear in the whole temperature range. The isosteric heats of adsorption depended only slightly on the amount adsorbed and surpassed the heat of vaporization. For the adsorption

branch we obtained a mean value of 11.31 kcal mol^{-1}, for the desorption branch a mean value of 11.64 kcal mol^{-1}. (The heat of vaporization of water at 0°C is 10.57 kcal mol^{-1}.) The linear course of adsorption isosteres indicated that there was not any phase transition similar to the liquid—solid phase transition in adsorbed water. This phase transition is characterized by a break on adsorption isosteres or a bend in a narrow interval of temperatures. Thus the adsorbed water remains in pores in a liquid state at temperatures lower than its melting point.

The existence of the adsorbed substances in an undercooled state was already described in the literature. A detailed analysis was given in papers [6—12]. It was shown that in equations of adsorption isotherms and in expressions for the calculation of thermodynamic functions changes, as a standard state an undercooled liquid phase instead of a solid equilibrium phase is to be used. That means that the adsorption would reach a limiting value only at the vapour pressure of an undercooled liquid; this value is naturally experimentally inaccessible as is the whole metastable region of supersaturated vapour. In the region of the high relative pressures the resulting adsorption isotherms possess open hysteresis loops (Fig. 1).

Discussion

When following the limit of the phase stability, the thermodynamic conditions of its stability with regard to the changes taking place without the formation of a new phase are to be determined. For a binary solution, *i.e.* for a system analogous to the adsorption system, these conditions are expressed by the inequalities

$$\left(\frac{\partial T}{\partial S} \right)_{V,n} > 0, \tag{1}$$

$$\left(\frac{\partial P}{\partial V} \right)_{T,} < 0, \tag{2}$$

$$\left(\frac{\partial \mu'}{\partial n} \right)_{T,P} > 0, \tag{3}$$

where T is temperature, S entropy of the solution, V its volume, P pressure, μ' the chemical potential of the solved substance, and n the number of its moles (the number of moles of the solvent is constant).

When the limit of stability is reached, the inequalities (1—3) change into equalities; this limit in the coordinates S, V, and n is univocally determined by these three equations. In the same way as with inequalities (1—3) it is possible to derive the inequality for the adsorption equilibria [13]

$$\left(\frac{\partial \mu}{\partial a} \right)_{T} > 0, \tag{4}$$

where μ is the chemical potential of the adsorbed substance and a the adsorbed amount.

If we denote

$$\Delta \mu = \mu - \mu^0(T), \tag{5}$$

where $\mu^0(T)$ is the chemical potential of adsorbate in the standard state, the inequality (4) can be written in the form

$$\left(\frac{\partial \Delta\mu}{\partial a}\right)_T > 0. \tag{6}$$

In the case of the studied system water—active carbon we have to choose the stable or metastable liquid phase as a standard state. The change of the chemical potential is given by equation

$$\Delta\mu = -A = -RT \ln p_{01}/p, \tag{7}$$

where p_{01} is the saturated vapour pressure of liquid water (undercooled below $-0°C$).

In Fig. 1 the adsorption isotherms of water vapour in coordinates A vs. a are shown. On the desorption branches of hysteresis loops appears an inflexion point where the inequality (4) changes into equality. Pressure p^+ and the adsorbed amount a^+ corresponding to this point thus indicate the limit of stability of the adsorbed phase. The value of adsorption at the relative pressure of 1 corresponds to the completely filled up micropores and mesopores [2]. The decrease of adsorption to the value a^+ is evidently caused by the desorption of water molecules from the volume of pores and this value itself represents then the limit of stability of that part of the adsorbed phase which is not under the influence of the walls of pores. For this reason, at pressure p^+ the adsorption does not drop to the zero value and the hysteresis loop is not yet closed either.

The adsorbed phase can be compared in some respects with the liquid phase; in this connection we can compare the limit of its stability with the limit of the bulk liquid phase. The chemical potential of the liquid at the limit of stability is given by equation

$$\mu_{c1} = \mu^0(T) + \int_{P_0}^{P_c} V \, dP, \tag{8}$$

where $P_0 = p_{01}$ is pressure of the liquid in equilibrium with the vapour, V is molar volume of the liquid, P_c is pressure at the stability limit, i.e. at the point where

$$\left(\frac{\partial P}{\partial V}\right)_T = 0. \tag{9}$$

If we put now

$$\mu_{c1} - \mu^0(T) = -A^+ = -RT \ln p_{01}/p^+, \tag{10}$$

we get

$$RT \ln p_{01}/p^+ = -\int_{P_0}^{P_c} V \, dP. \tag{11}$$

If we neglect the dependence of the molar volume V on pressure P and the value of P_0 with respect to that of P_c (for most liquids pressures P_c reach considerable
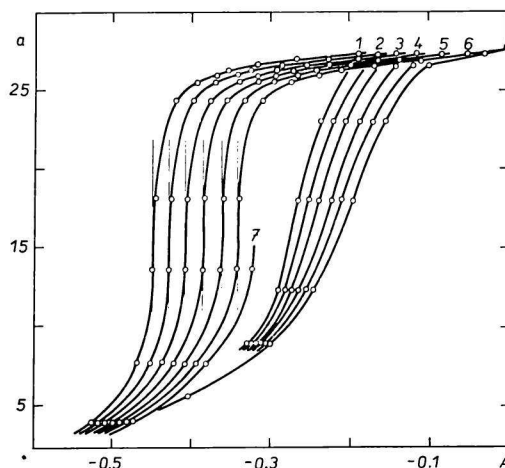
Fig. 1. Adsorption isotherm of water vapour on active carbon in coordinates A (kcal mol^{-1})
vs. a (mmol g^{-1}).

Isotherms *1—7* correspond to temperatures -30, -20, $+30°$C.
In the inflection points of desorption branches the tangents are plotted.

negative values at room temperatures), eqn (*11*) is modified, and on rearrangement
gives

$$P_{\mathrm{c}} \doteq P^+ = -\frac{RT \ln p_{01}/p^+}{V}. \tag{12}$$

This equation derived in a slightly different way was used in [3]. Its application
requires the knowledge of the value P_{c}; on the other hand, the application of the
eqn (*11*) is contingent on the knowledge of the data of state of liquid in the meta-
stable region.

It is rather difficult to obtain an experimental data on the behaviour of liquid
far in the metastable region where the pressures P reach considerably negative values.
It is evidently impossible to obtain a direct information on the limit of stability
since this limit corresponds to the complete loss of stability to return to the original
state at any deviation from this state. A series of approximation methods of thermo-
dynamic functions of liquids in metastable region was proposed in the literature
(cp. *e.g.* the review [14]). For the calculation of the data of state the Himpan equa-
tion [15] containing four constants f_{a}, f_{b}, f_{c}, and f_{d} was recommended

$$\pi = \frac{\epsilon \tau}{\varphi - f_{\mathrm{d}}} - \frac{f_{\mathrm{a}}}{(\varphi - f_{\mathrm{b}})(\varphi \tau - f_{\mathrm{c}})}. \tag{13}$$

In this equation $\pi = P/P_k$, $\varphi = V/V_k$ and $\tau = T/T_k$ stand for the reduced values
of pressure, volume, and temperature, respectively (indexes k denote the critical
constants), and $\epsilon = RT_k/P_k V_k$. The constants f_{a} through f_{d} for different substances
were determined by Himpan from critical constants and from experimental data
of state of liquid phase. According to eqn (*13*) chemical potential of the liquid at
the limit of stability is given by equation

$$(\mu_{cl})_H = \mu^0(T) + P_k V_k \int_{\pi_0}^{\pi_0} \varphi \, d\pi = P_k V_k \left[\frac{\epsilon \varphi \tau}{\varphi - f_d} - \frac{f_a \varphi}{(\varphi - f_b)(\varphi \tau - f_c)} - \right. \tag{14}$$

$$\left. - \epsilon \tau \ln (\varphi - f_d) + \frac{f_a}{\tau f_b - f_c} \ln \frac{\varphi - f_b}{\varphi \tau - f_c} \right]_{\varphi_0}^{\varphi_c}$$

where the reduced pressure or volume of liquid in equilibrium with the vapour and at the limit of stability, respectively, is differentiated by indexes 0 and c (H designates the calculations according to Himpan equation). In Table 1 the changes of chemical potential $(\Delta\mu_{cl})_H = (\mu_{cl})_H - \mu^0(T)$, experimental quantities A^+, pressures P^+ calculated according to the relation (12), and pressures $(P_c)_H$ determined according to the Himpan equation and the condition (9) for the whole range of temperatures investigated are presented. The values $(\Delta\mu_{cl})_H$ are always lower than the values A^+, pressures P^+ are always higher than pressures $(P_c)_H$. From these differences it follows that the limit of stability of water in the pores of active carbon differs considerably from the value found by means of Himpan equation. One would expect that the temperature dependence of the quantity A^+ will be described by Himpan equation, i.e. that the ratio

$$\frac{A^+}{(\Delta\mu_{cl})_H} = K \tag{15}$$

will be constant. As evident from Table 1, the constant K does not depend on temperature within the experimental errors, however, the value A^+ represents only 16% of the change of chemical potential $(\Delta\mu_{cl})_H$.

Equation (11) and the consequent expression (12) hold only provided that the behaviour of the substance in the adsorbed phase corresponds to the behaviour of the bulk phase. Himpan equation applied to the calculation of the data of state of the liquid phase should be regarded as an approximation formula for the calculation of the limit of stability of liquids. When using other method of approximation

Table 1

Comparison of the limit of stability of water in the bulk liquid phase with the limit of stability of water in capillary-condensed phase

t °C	$(\Delta\mu_{cl})_H$ kcal mol^{-1}	A^+ kcal mol^{-1}	$(P_c)_H$ atm	P^+ atm	K
−30	−2.820	−0.450	−6190	−1020	0.160
−20	−2.666	−0.430	−5820	−919	0.161
−10	−2.530	−0.409	−5490	−935	0.162
0	−2.399	−0.386	−5190	−885	0.161
10	−2.278	−0.362	−4900	−830	0.159
20	−2.160	−0.342	−4620	−782	0.158
30	−2.043	−0.323	−4360	−737	0.158
					$\bar{K} = 0.160$

[16, 17], or another equation of state [18], we obtain the values of pressure P_c always considerably lower than the pressure P^+. Thus it may be assumed that in the vicinity of the limit of stability it is impossible to substitute the behaviour of the adsorbed water for the behaviour of the bulk phase. This is to be considered *e.g.* in the calculation of radii of pores from an isotherm of water vapour by means of Kelvin equation.

The condition

$$\left(\frac{\partial \mu}{\partial a}\right)_T = 0 \tag{16}$$

used for the determination of pressure P^+ need not always be related to the limit of stability of the adsorbed phase. In the case of adsorbents containing mesopores in a very narrow interval of radii the vertical decrease of adsorbed amount on the desorption branch of the hysteresis loop can be caused by the emptying of pores filled with the capillary condensed liquid. The pressure P^+ can thus be considered to be a limit of stability only in those cases where its value is given by the adsorbate and does not depend on the adsorbent.

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