On the mechanisms of phenol adsorption by carbons

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The removal of phenol and related compounds from dilute aqueous solutions by activated carbons corresponds to the coating of the micropore walls and of the external surface by a monolayer. This process is described by an analog of the Dubinin—Radushkevich—Kaganer equation. On the other hand, as suggested by immersion calorimetry at 293 K, in the case of concentrated solutions, the mechanism corresponds to the volume filling of the micropores, as observed for the adsorption of phenol from the vapor phase. The equilibrium is described by the Dubinin—Astakhov equation. It follows that the removal of phenol from mixtures with water depends on the relative concentrations, and the limiting factor for adsorption is either the effective surface area of the carbon, or the micropore volume.

Key words: adsorption, phenol, activated carbons, surface area, microporosity, immersion calorimetry.

The removal of phenol from aqueous solutions is of great industrial importance and a number of studies have been devoted to this topic, for example, the recent review.[1] Activated carbon is a popular adsorbent and it appears that the adsorption equilibrium for phenol and related compounds corresponds to a classical type I isotherm, characterized by a limiting amount N_{am} (mmol g^{-1}). This amount depends on the carbon and on the state of its surface, since it has been shown that an increase in the amount of oxygen-containing complexes reduces the sorptive capacity.

Until recently, most studies were focused on the classical equations of Langmuir, Freundlich, or Redlich[2] but these expressions contain parameters that cannot be used to predict adsorption at other temperatures. On the other hand, it has been shown that Dubinin′s theory, originally developed for the adsorption of vapors by microporous solids, can be transposed to the description of adsorption from aqueous solutions.[3,4] This property is due to the fact that carbons are essentially hydrophobic and display a strong affinity for organic molecules. Consequently compounds such as phenol, which have a limited solubility in water, will be adsorbed preferentially from aqueous solutions. The same also applies to certain hydrophobic zeolites.

In the case of phenolic compounds, the comparison with non-porous carbon blacks indicates clearly that adsorption is limited to a single layer on the open surface and on the walls of the micropores. The combination of adsorption measurements with the enthalpy of immersion of porous and non-porous carbons into solutions containing enough phenol to avoid depletion shows that the molar energy of transfer is about −31 kJ mol^{-1} in all cases.[4,5] This is a clear indication that the mechanisms are the same in both cases and the relevant parameter for the removal of phenol (and related compounds) is the surface area of the carbon, consisting of the micropore walls and the external surface area, rather than the micropore volume.

This mechanism corresponds to the removal of phenol from water, where it is often an unwanted impurity, as found in practice. However, although its solubility in water is limited, phenol can also form concentrated solutions when relatively small amounts of water are added to the solid at room temperature. As shown in the present study, for this type of solution the selective adsorption of phenol by active carbons corresponds to the mechanism of micropore filling. This means that the micropore volume becomes the relevant parameter for the prediction of the adsorption equilibrium, as observed for the adsorption of pure phenol from the vapor phase.

Fundamentals of Dubinin′s theory

Adsorption by microporous solids such as activated carbons and zeolites is described by Dubinin′s theory. In the modern formalism, its basic relation is the so-called Dubinin—Astakhov equation (DA)[6—9]

$$N_a = N_{a0}\exp(-A/E)^n, \qquad (1)$$

where N_a represents the amount adsorbed at relative pressure p/p_s, N_{a0} is the limiting amount filling the micropores and $A = RT\ln(p_s/p)$. The latter is a thermodynamic potential and $A = -\Delta G_{ads}$, the reference being the saturated vapor at T and p_s. Since Eq. (1) reflects the filling of a volume, it is convenient to replace the limiting amount N_{a0} by the micropore volume $W_0 = N_{a0}V^a_m$, where V^a_m is the molar volume in the adsorbed state at the given temperature. As a first and usually good approximation, one may use the molar volume in the

liquid state. Exponent $n = 2$ corresponds to the classical Dubinin—Radushkevich equation (DR) and E is the so-called characteristic energy of the system. It depends on the adsorbent and on the adsorptive but one may write that $E = \beta E_0$, where β is a coefficient depending only on the adsorptive. By convention, benzene is the reference and $\beta(C_6H_6) = 1$. Values of β have been tabulated for adsorption by microporous carbons and relations have been proposed for their calculation.[10]

Equation (1) is based on the thermodynamic potential $A = RT\ln(p_s/p)$, and it can be shown[8,9] that the enthalpy of immersion of a microporous solid into a liquid, whose vapor is adsorbed follows Eq. (1), is given by

$$\Delta H_i = -\beta E_0(W_0/V_m)(1 + \alpha T)\Gamma(1 + 1/n) + h_iS_e. \quad (2)$$

In this expression, α is the expansion coefficient of the liquid, $\Gamma(1 + 1/n)$ is the tabulated gamma function, and h_i (J m^{-2}) is a negative quantity like ΔH_i (J g^{-1}), which represents the wetting of the external surface area of the solid, S_e. The latter is conveniently derived from comparison plots based on the adsorption of standard adsorbates N_2 (77 K), C_6H_6 (293 K), or CO_2 (273 K).[11] In the case of the DR equation, one obtains

$$\Delta H_i = -\beta E_0 W_0(1 + \alpha T)\pi^{0.5}/(2V_m) + h_iS_c. \quad (3)$$

Dubinin´s theory is not limited to the volume filling of micropores.[12] The modified form of Eq. (1) is named the Dubinin—Radushkevich—Kaganer (DRK) equation and describes adsorption on non-porous surfaces

$$N_a = N_{am}\exp(-A/E)^2, \quad (4)$$

where N_{am} represents the monolayer capacity of the surface. The temperature invariance of the characteristic energy of the DRK equation (4) has been tested for a few systems.[13,14] It has also been shown that the selective adsorption from aqueous solutions can be described by a modified version of Eq. (4), where relative pressures are replaced by relative concentrations. With the present formalism, one obtains

$$N_a = N_{am}\exp\{-[RT\ln(c_s/c_{eq})/E_s]^2\}, \quad (5)$$

where E_s is the characteristic energy of the given system and c_s represents the saturation concentration at temperature T.

It has been shown that in the case of phenol and related compounds, the following equation applies near room temperature[4]

$$N_a = N_{am}\exp\{-[RT\ln(c_s/c_{eq})/\beta_s E_{0s}]^4\}. \quad (6)$$

With respect to Eq. (5), the higher exponent ($n = 4$) extends the domain of validity from $1 \cdot 10^{-3} < c_{eq}/c_s < 1$ to $4 \cdot 10^{-4} < c_{eq}/c_s < 1$.

Carbons being essentially hydrophobic, their enthalpy of immersion into aqueous solutions of phenol corresponds to the selective adsorption of this molecule by the solid in the form of a monolayer on the walls of the micropores and on the non-porous (external) surface. However, as discussed below, in the case of phenol containing enough water to liquidize it at room temperature, the adsorption process is no longer limited to a layer but corresponds to the filling of the micropore volume W_0.
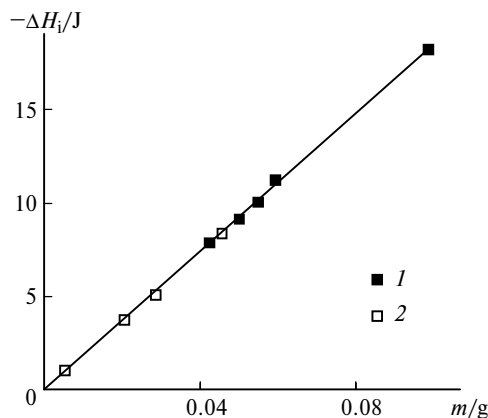
Experimental

The present study is based on 14 well-characterized microporous carbons[4,5,8] (**1—14**) and on two non-porous carbons blacks, N-234-G (92 m^2 g^{-1}) and Vulcan3-G (71 m^2 g^{-1}).

The techniques for adsorption from the vapour phase and from solutions are described in detail elsewhere,[4,8] as well as immersion calorimetry. In the latter techniques, samples of 0.04—0.1 g of carbons were immersed into phenol containing 25 (in some cases, 15) wt.% water in order to check for a possible influence of the water concentration on ΔH_i (no difference was observed). As a typical example, Fig. 1 shows the enthalpies of immersion of carbon **13** (see Table 1) into solutions of phenol containing 15 and 25 wt.% water. It is seen that the enthalpies are almost identical and increase proportionally with the amount of carbon. The slope of the plots gives $\Delta H_i(PhOH)_{exp} = -184.4\pm5$ J g^{-1}.

In order to complete the study, it was also decided to examine the adsorption of phenol vapor at 303 K on microporous carbon **7**. The vapor was provided by pure phenol kept near 285 K, and measurements were taken at 306 and 319 K, in the range of relative pressures $0.001 < p/p_s < 0.26$. Two temperatures were considered in this preliminary work, in order to verify that the principle of temperature invariance of parameter E is fulfilled. The present experiments were considered to be sufficient for the determination of parameters N_{a0} and E. The latter leads to $\beta(PhOH)$ of the DR equation, E_0 being known from routine characterizations of the carbon with benzene and other vapors.

Results and Discussion

As shown elsewhere,[4,5] the enthalpy of immersion of the carbons into aqueous solutions of phenol 0.4 M and the corresponding isotherms analyzed with Eqs. (5) and (6) lead to the true surface area, consisting of the

Fig. 1. Experimental enthalpies of immersion (ΔH_i) at 293 K for adsorption on carbon **13** of phenol from solutions containing 15 (*1*) and 25% (*2*) water as a function of the mass of carbon (*m*). The slope corresponds to an average value of 184.4±5 J g^{-1}.

Table 1. Structural characteristics of the microporous carbons and their enthalpies of immersion at 293 K into benzene and solutions of phenol containing 25% H_2O

Carbon	$E_0 W_0$ /kJ cm^3 mol^{-1} g^{-1}	S_e /m^2 g^{-1}	$\Delta H_i(C_6H_6)_{exp}$	$\Delta H_i^{mi}(C_6H_6)$	$\Delta H_i^{mi}(C_6H_6)_{calc}$	$\Delta H_i(PhOH)_{exp}$	$\Delta H_i^{mi}(PhOH)$
					J g^{-1}		
1	1.32	120	29.5	15.9	17.9	39.1	23.6
2	4.21	212	81.5	57.3	57.2	93.5	66.2
3	10.50	35	148.1	144.1	142.6	161.0	156.5
4	8.60	105	126.6	114.6	116.8	143.4	129.9
5	7.26	250	127.2	98.7	98.5	144.7	112.5
6	6.95	113	106.7	93.8	94.3	132.0	117.4
7	11.97	90	172.9	162.6	162.5	177.6	166.0
8	11.08	26	149.0	146.0	150.4	191.4	188.0
9	10.62	157	160.0	142.1	144.2	172.4	152.1
10	9.24	110	137.8	125.3	125.5	163.7	149.5
11	10.85	45	168.2	163.1	147.3	197.4	191.6
12	7.06	28	92.0	88.8	95.8	112.2	108.6
13	10.76	50	149.6	143.9	146.0	184.4	178.0
14	2.77	119	53.6	40.0	37.6	52.6	37.2

micropore walls and the external surface area S_e. It appears that the molar energy of transfer of phenol from the solution onto the surface, $\Delta H_i/N_{am}$ varies between -30 and -32 kJ mol^{-1} for porous and non-porous carbons alike. This justifies the use of the specific enthalpy of immersion $h_i(PhOH) = -0.109\pm0.008$ J m^{-2} obtained for carbon black N-234-G to calculate the real surface of carbons from their enthalpy of immersion. A similar approach has been used earlier with caffeine,[5,8] another molecule with a limited solubility in water and a high affinity for carbon. The corresponding specific enthalpy $h_i(caffeine) = -0.113\pm0.001$ J m^{-2} but in view of its dimensions this molecule cannot penetrate into micropores of less than 0.5—0.6 nm.

In the case of the concentrated phenolic solutions used in the present study (phenol+25% water w/w), carbon blacks N-234-G and Vulcan 3-G lead to a specific enthalpy of -0.129 ± 0.009 J m^{-2}. The difference with the case of dilute solutions may be ascribed to the effect of the bulk of the solution and the high affinity of phenol for the surface of carbons.

It appears that the enthalpies of immersion of the microporous carbons into the concentrated solutions are generally larger than observed for the dilute solution. For example, in the case of carbon **13** shown in Fig. 1, one obtains enthalpies of 184.4±5 J g^{-1} (phenol with 15 to 25% water) and 113.5±6 J g^{-1} (0.4 *M* phenol in water). For the different carbons of Table 1, the ratios vary between 1 and 2.1, and no trend can be detected. The increase in ΔH_i suggests therefore a change in the mechanism of adsorption from the two types of solutions. Accordingly, we considered an approach based on the hypothesis of the filling of the micropore volume by phenol in the case of the concentrated solution, with the coating of the external surface S_e by phenol.
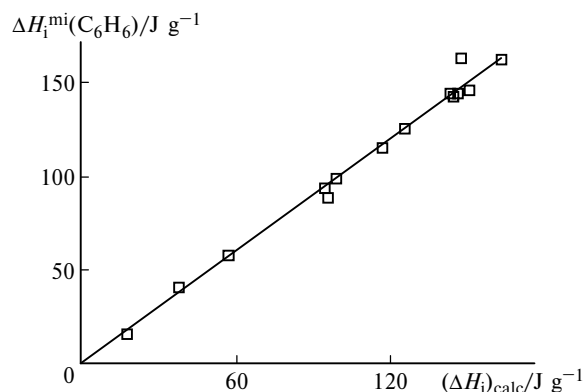
For the given carbons, the micropore filling process itself was first tested by examining their enthalpies of immersion into benzene at 293 K. The experimental
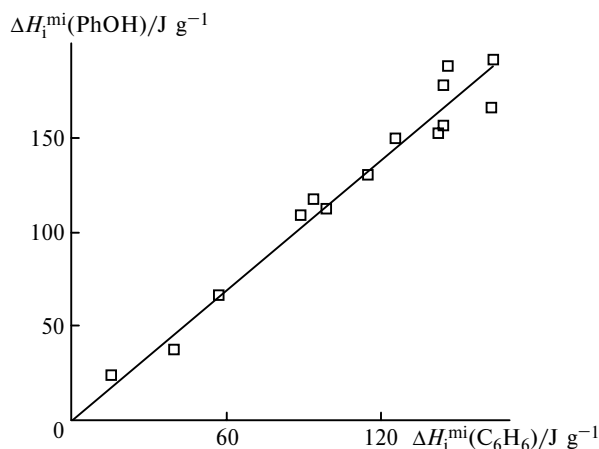
values $\Delta H_i(C_6H_6)_{exp}$ were corrected for the wetting of the external surface area, which corresponds to -0.114 J m^{-2} for benzene at 293 K.[8] According to Eq. (3), the enthalpy of immersion in the micropores alone (ΔH_i^{mi}/J g^{-1}) is given by

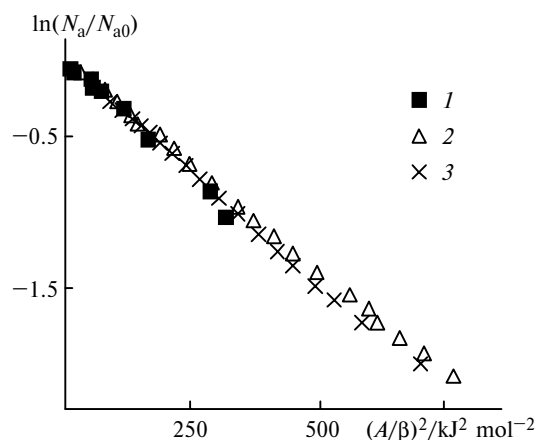$$\Delta H_i^{mi} = -\beta E_0 W_0 (1 + \alpha T)\pi^{0.5}/(2V_m). \quad (7)$$

and the right-hand side of Eq. (7) can be calculated from $E_0 W_0$ (Table 1), α ($1.24 \cdot 10^{-3}$ K^{-1}), and V_m (88.91 cm^3 mol^{-1}). As shown in Fig. 2, one obtains an excellent agreement between $\Delta H_i^{mi}(C_6H_6)$ and the value predicted by Eq. (7). The slope is equal to 1.00±0.01, which is a test of self-consistency.

Using the same approach for immersion into concentrated phenol solutions, one obtains the enthalpy of immersion expected for the filling of the micropores alone, $\Delta H_i^{mi}(PhOH)$, by applying a correction of -0.129 J m^{-2} for the wetting of the external surface S_e. As shown in Fig. 3, one observes a very good correlation

Fig. 2. Comparison of the experimental enthalpies of immersion calculated by Eq. (7) with the enthalpies of immersion $\Delta H_i^{mi}(C_6H_6)$ determined experimentally for the micropore filling of carbons **1—14** by benzene. The slope is 1.00±0.01.

$\Delta H_i^{mi}(PhOH)/J\ g^{-1}$

Fig. 3. Comparison of the enthalpies of immersion for the micropore filling of carbons **1—14** at 293 K by phenol and $\Delta H_i^{mi}(PhOH)$ and benzene $\Delta H_i^{mi}(C_6H_6)$. The slope is 1.15±0.02.

$\ln(N_a/N_{a0})$

Fig. 4. The DR plot for the adsorption on carbon **7** from the vapor phase of phenol at 306 and 319 K (*1*) and C_6H_6 (*2*) and CH_2Cl_2 (*3*) at 293 K.

between $\Delta H_i^{mi}(PhOH)$ and $\Delta H_i^{mi}(C_6H_6)$. This agreement suggests that the enthalpy of immersion into the solutions of phenol effectively corresponds to a process of micropore filling. The slope of 1.15±0.02 leads to a value of 0.0156±0.0003 mol cm^{-3} for $\beta(1 + \alpha T)\pi^{0.5}/(2V_m)$ of phenol.

As illustrated by Fig. 4, the adsorption of phenol vapors by carbon **7** at 306 and 319 K follows the Dubinin—Radushkevich equation like, for example, benzene and dichloromethane at 293 K. The best fit of the data corresponds to an affinity coefficient $\beta(PhOH) = 1.0$. It is in good agreement with the value of 1.06 predicted by using the ratio of the parachors of phenol and benzene, a relatively good approximation for the calculation of β.[6,10] From the limiting value for the adsorption of phenol, $N_{a0} = 6.97$ mmol g^{-1} and the micropore volume of the carbon **7**, $W_0 = 0.64$ cm^3 g^{-1}, one obtains a molar volume of 90 cm^3 mol^{-1} for phenol in the adsorbed state at 306 K. This value is close to the volume of 89 cm^3 mol^{-1}

for the liquid at the same temperature. If one uses, as first approximation, the expansion coefficient of liquid phenol at 323 K ($\alpha = 0.83$ K^{-1}) and the extrapolated molar volume of the liquid (87.3 cm^3 mol^{-1}), $\beta\alpha(1 + T)\pi^{0.5}/(2V_m) = 0.0128$ mol cm^{-3} at 293 K. It is smaller than the value obtained from the comparison between the enthalpies of immersion $\Delta H_i^{mi}(PhOH)$ and $\Delta H_i^{mi}(C_6H_6)$ but the difference does not question the volume filling of the micropores. On the other hand, it shows that the enthalpy of immersion is systematically larger than expected for pure phenol on the basis of the data obtained from its isotherm. This may be due to the fact that in the present experiments phenol contains 15 to 25% water. As the mixture is endothermic, it is reasonable to postulate that de-mixing increases the enthalpy of immersion by a factor proportional to the amount of phenol filling the micropores and leaving water outside. It is also possible that the expansion coefficient of phenol in the adsorbed state is larger than expected. These possibilities will be examined in detail later.

In conclusion, the present study indicates that the adsorption of phenol from concentrated aqueous solutions corresponds to a process of micropore filling and that it is not limited to the coating of the micropore walls, as observed for dilute solutions. This means that, in the case of phenol, depending on its concentration, two distinct mechanisms have to be considered for its selective adsorption by active carbons.

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