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Calculation of Protolytic Equilibria Parameters on a Surface of Some Carbon Adsorbents According to Potentiometric Titration Data

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Constants and Gibbs energy values of neutralization were calculated for protolytic equilibria on carbon adsorbents based on anthracite, charcoal and brown coal. A proposal regarding composition of surface functional groups of these sorbents was made.

Keywords: Activated Carbon, Protolytic equilibria, Adsorption properties, Chemical Structure, Surface Properties.

Introduction

An investigation of acid-base characteristics of adsorbents is a matter of practical interest, since they are involved into the technological schemes for separation and concentration of metal ions. It is known that adsorbents synthesized on the basis of natural materials show a high selectivity to individual components during recovery from solutions [1]. We have already shown that the natural oxidized coals of Kuznetsk and Kansk-Achinsk deposits of Siberia are promising to be used as a basis for synthesis of sorbents, which can selectively recover some non-ferrous metal ions and iron (III) from industrial manganese sulfate solutions [2]. That is why the presentation of equilibrium phenomena on a surface of such sorbents is important for investigators. It should

be noted that a number of publications related with this question is rather limited [2-4].

A consideration of acid-base characteristics of sorbents is frequently accomplished with data of potentiometric titration of samples by acid and (or) base [5]. The particular values of dissociation constants and of surface concentration of reaction centers (RC) are obtained by a treatment of a potentiometric titration curve within the limits of any model of acid-base equilibrium in the system "solution – sorbent". For instance, a widespread approach to calculation of RC ionization constants \overline{K}_a ¹



is based on the Henderson's equations [5]:

$$p\overline{K}_a = pH - \lg \frac{\alpha}{1-\alpha} \quad (2)$$

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² Here and further, the line over the symbol indicates the sorbent phase.

or

$$p\overline{K}_a = pH - m \lg \frac{\alpha}{1-\alpha}, \quad (3)$$

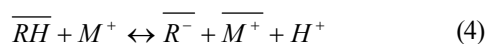
where α is the neutralization degree of the adsorbent;

m is tangent of the slope angle of a curve plotted

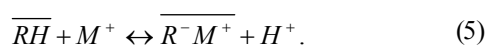
on the coordinates $pH = f(\lg \frac{\alpha}{1-\alpha})$; the value of

m characterizes a force of electrostatic interaction between functional groups (reaction centers).

However, the $p\overline{K}_a$ calculation in accordance with equations (2) and (3) implies that $pH = p\overline{H}$. Such assumption is in conflict with both the theoretical representations and experimental data [6]. In our opinion, it is hardly possible to determine the $p\overline{K}_a$ values directly, i.e. using only the potentiometric titration data, because in this case the additional information concerning the pH values of solution in the sorbent micropores is required. That is why we consider that an alternative approach to the estimation of acid-base properties is quite reasonable. Our approach is based on use of exchange equilibrium constants $K = K_{H/M}$ in accordance with the following equations:



or



These equations present two limiting cases for the state of counter-ions M^+ in the sorbent phase [7]. The state of a strong bonding (fixing) of counter-ions in a dense part of double electric layer (DEL) and in Stern layer is described in (5). But if the counter-ions are able to move freely in the surface gel film, in this case the chemical interactions correspond to the equation (4), which includes a mobile ion (MI) in sorbent phase.

The present paper is focused on calculation of the exchange constants using the equation

(4) and (5), i.e. we have used both models – MI and DEL, aiming to ascertain, which of the limiting cases is the closest to the real state of the adsorption layer.

Experimental

We have investigated the carbon adsorbents synthesized on the basis of brown coals from Kansk-Achinsk deposit (AUIS), anthracite from Kuznetsk deposit (LKAU-2 and LKAU-7) and industrial charcoal made in Perm region (BAU). All the adsorbents were synthesized from coals according to the following technological scheme: preparation, carbonization (600-640°C), activation of the carbonized material in a steam-gas medium at 830-850°C with the further modification by air oxygen at 400-410°C.

The conditioning of sorbents was carried out by their alternate treatment by HCl and NaOH solutions (each of 5%) and by 10% ammonia solution. The metal content in the conditioned sorbents was determined by titration with EDTA in solutions obtained after desorption of mineral impurities (desorbent – 0.1 M HCl, exposure time – 72 h). This content does not exceed 0.03 mmol per 1 g of sorbent.

The physical-chemical characteristics of the carbon adsorbents investigated are presented in Table 1.

The potentiometric titration of sorbents in H^+ -form was carried out at $(25 \pm 0.5)^\circ\text{C}$ by method of individual weighed samples [5] using 0.01 M and 0.1 M NaOH as a titrant in the presence of NaCl as a background electrolyte (the ionic strength I was about 1). The pH^* values (see below) were measured using universal ionometer EV-74 (Russia). The experimental error was in this case not more than 0.03 logarithmic units.

The integral potentiograms of the sorbents were plotted on the coordinates

$$E = f(pH),$$

Table 1. Physical-chemical characteristics of carbon adsorbents investigated

Trade name	Basis for synthesis	Specific surface area (m ² /g)	Total pore volume (cm ³ /g)	Sorption capacity for	
				I ₂ (mmol/g)	methylene blue (mg/g)
AUIS	Brown coal	420	0.38	3.4	25
LKAU-7	Anthracite	680	0.86	4.8	29
LKAU-2	Anthracite	600	–	4.5	–
BAU	Charcoal	530	1.20	6.0	47

where E is sorption capacity to Na^+ ions (mmol/g) and

$$pH = pH^* + \lg \gamma,$$

where pH^* is pH value measured (see above);

γ is a coefficient of activity for H^+ (H_3O^+) ions:

$$\lg \gamma = -0.5I^{1/2}/(1 + 3.29aI^{1/2}) - bI. \quad (6)$$

In accordance with the work [8], for $I = 1$ M NaCl, $a = 4.20$; $b = 0.22$; $\lg \gamma = -0.25$.

The differential potentiograms were plotted by methods of numerical differentiation in approximation

$$\frac{dE}{dpH} \approx \frac{\Delta E}{\Delta pH} = \frac{E_{i+1} - E_i}{pH_{i+1} - pH_i}, \quad (7)$$

where E_i and pH_i are exchange capacity and pH value in experimental point i , respectively.

All the results were processed statistically according to the standard methods [9] for $n = 3$ and $p = 0.95$.

Results and Discussion

Fig. 1 presents the integral potentiograms of the carbon adsorbents investigated. These curves have some (n) inflection points, and the differential potentiograms (Fig. 2), accordingly, show n peaks. Therefore, these experimental data can be interpreted within the law of mass action for n types of RC:

$$E = f(pH) = \sum_{i=1}^n \frac{K_{ci}[Na^+]E_{oi}}{K_{ci}[Na^+] + \varphi(pH)}, \quad (8)$$

where K_{ci} is exchange concentration constant for RC of type i ;

E_{oi} is exchange capacity of RC of type i ;

$[Na^+]$ is equilibrium concentration of Na^+ ions in solution, mmol/mL;

$\varphi(pH)$ is a parameter determined by a neutralization model chosen for study. In approximation of DEL model (see equation (5)):

$$\begin{cases} \varphi(pH) = E \cdot 10^{-pH}; \\ K_{ci} = K_{ii}\gamma(Na^+)/\gamma(H^+); \end{cases} \quad (9)$$

where K_{ii} is thermodynamic equilibrium constant;

$\gamma(Na^+)$ and $\gamma(H^+)$ are coefficients of activity for Na^+ and H^+ ions, respectively.

In approximation of MI model (see equation (4)):

$$\begin{cases} \varphi(pH) = 10^{-pH}; \\ K_{ci} = K_{ii}\gamma(Na^+)/\gamma(H^+). \end{cases} \quad (10)$$

Within the scope of DEL model, the values of pK_{ci} and E_{oi} are calculated assuming the following simplifications:

- $\gamma(Na^+)/\gamma(H^+) \approx 1$, $[Na^+] \approx 1$;
- overlaps of RC neutralization processes can be neglected.

$$\begin{cases} E = f(pH) \approx K_{ci}[Na^+] \frac{E_{oi}}{K_{ci}[Na^+] + \varphi(pH)} + \\ + \sum_{j=1}^{i-1} E_{oj}, i = 2, 3, \dots, n \\ pH \in [pH_i; pH_{i+1}] \end{cases} \quad (11)$$

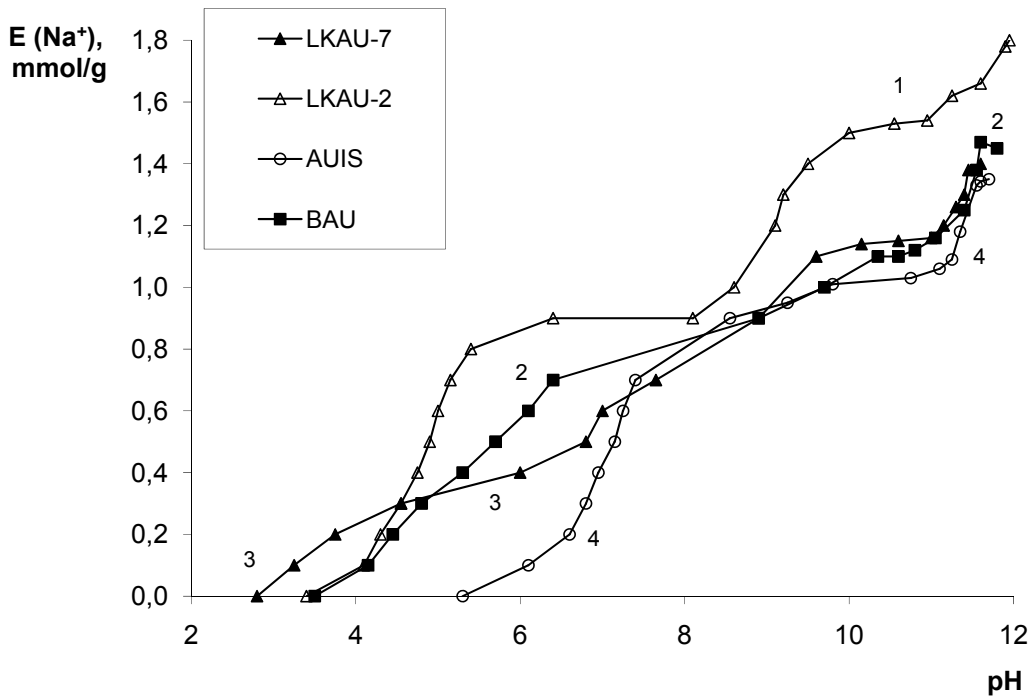


Fig. 1. Integral potentiograms of carbon adsorbents. 1 – LKAU-2; 2 – BAU; 3 – LKAU-7; 4 – AUIS

where pH_i and pH_{i+1} are the points of i and $(i+1)$ minima of the differential potentiogram (Fig. 2).

It should be noted that the simplifying assumption (b) is verified after processing experimental results, since the exchange capacity value for RC of i type in the interval $pH \in [pH_{i-1}; pH_i] \cup [pH_{i+1}; pH_{i+2}]$ does not exceed 0.03–0.04 mmol/g, i.e. these values are comparable with the error of capacity determination.

In accordance with the equation (11), the curve $E = f(pH)$ is approximated on each interval $pH \in [pH_i; pH_{i+1}]$ by the following dependencies:

$$\begin{cases} pK_{ii} = pH - \lg(\alpha_i / (1 - \alpha_i)) \\ \alpha_i \approx \frac{E(pH) - E(pH_i)}{E(pH_{i+1}) - E(pH_i)} \end{cases} \quad (12)$$

We have used the MI model only for the calculation of concentration equilibrium constants, because the thermodynamic constant can not be calculated without the coefficients of activity $\bar{\gamma}(Na^+)$ in sorbent phase. But

this calculation is unachievable, since well-substantiated theory of activity coefficients is not developed yet [10]. That is why the pK_{ci} values are calculated assuming (a) and (b) as well as c) $\bar{\gamma}(Na^+) / \bar{\gamma}(H^+) \cdot \bar{\gamma}(Na^+) \approx const$, $pH \in [pH_i; pH_{i+1}]$.

Within the scope of MI model, the curve $E = f(pH)$ is approximated on each interval $pH \in [pH_i; pH_{i+1}]$ by the following expression:

$$\lg E + pK_{ci} = pH - \lg(\alpha_i / (1 - \alpha_i)). \quad (13)$$

The equilibrium constants values, obtained by statistical processing of experimental data according to (12) and (13), are presented in Table 2. It can be seen from Table 2 that the standard deviation S for the constants calculated within MI model is higher than for constants based on DEL model. Therefore, it can be concluded that DEL model fits the experimental data better. Moreover, it is likely that the sodium ions are mainly fixed in a surface layer. Indeed, the migration of counterions can be discouraged by the following factors:

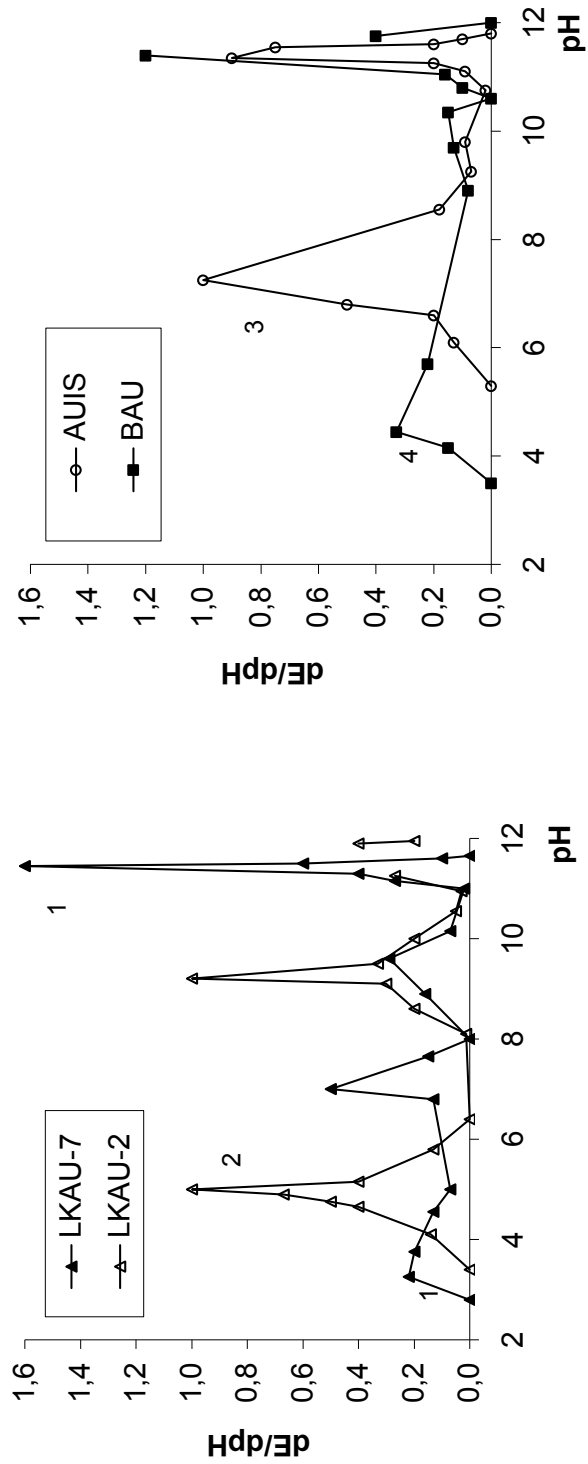


Fig. 2. Differential potentiograms of carbon adsorbents. 1 – LKAU-7; 2 – LKAU-2; 3 – AUIS; 4 – BAU

Table 2. Parameters of protolytic equilibria on a surface of carbon adsorbents investigated

Trade name	RC type (<i>i</i>)	E_0 for RC of <i>i</i> type, (mmol/g)	Total ($\sum_i E_{oi}$) concentration (total ($\sum_i E_{oi} / S$) concentration) (mmol/m ²)	DEL model		MI model		Gibbs energy ΔG_{298}^0 (kJ/mol) calculated by	
				pK_{Ti}	Dispersion S^2	pKa_i	Dispersion S^2	MPE	RA
LKAU-2	1	0.90	1.80 ($3.0 \cdot 10^{-3}$)	4.91	0.01	5.31	0.30	+41.77	+42.64
	2	0.64		8.99	0.04	8.88	0.08		
	3	0.26		11.64	<0.01	11.42	0.01		
LKAU-7	1	0.40	1.40 ($2.0 \cdot 10^{-3}$)	3.74	0.01	4.59	0.04	+41.75	+41.39
	2	0.45		7.15	0.02	7.37	0.04		
	3	0.31		9.01	<0.01	8.95	0.04		
	4	0.24		11.50	0.70	11.37	1.08		
AUIS	1	1.06	1.35 ($3.2 \cdot 10^{-3}$)	7.16	<0.01	7.63	0.10	+45.55	+47.13
	2	0.29		11.06	0.90	10.97	1.05		
BAU	1	0.90	1.47 ($2.8 \cdot 10^{-3}$)	5.41	0.10	5.87	0.21	+43.26	+43.40
	2	0.20		10.35	–	10.30	–		
	3	0.37		11.40	0.03	11.30	0.09		

- hydrophobic surface of carbon adsorbents;
- effect of RC electrostatic field at low surface concentration (see Table 2);
- steric impediments.

It should be noted that, on the one hand, in some cases the S^2 values are expressed by relatively large magnitudes: 0.70 and 0.90 for weak acidic RC ($pK \sim 11$ – 12) of LKAU-7 and AUIS, respectively (Table 2). On the other hand, the pK values calculated according to the equation (12), decrease in these cases with the increase in the neutralization degree α (Fig. 3). That can be caused by electrostatic interaction between the reaction centers or by exhibition of sorbents inhomogeneity effect [11].

Aiming to express the experimental data more adequately, we have used the Henderson's equation (3) with $m \neq 1$ here. For LKAU-7 we have determined $m = 0.113$; $pK_a = 11.34$ and for AUIS $m = 0.145$; $pK_a = 11.38$ (S^2 values do not exceed 0.01 in this case).

The data obtained allow to calculate some thermodynamic characteristics of the equilibria investigated, in particular, the Gibbs energy of neutralization ΔG_T^0 . Within the DEL model, the Gibbs energy can be calculated as a sum of partial values (method of partial energy – MPE) [12]:

$$\Delta G_T^0 \approx 2.3RT \sum_{i=1}^n pK_{Ti} E_{oi} / \sum_{i=1}^n E_{oi} \quad (14)$$

or using the model of inhomogeneous sorbents (Roginskiy's approximation – RA) [13].

For inhomogeneous sorbents [7], the potentiogram is approximated by the expression obtained by means of a limiting process at $n \rightarrow \infty$ in equation (8):

$$E = f(pH) = \int_{-\infty}^{+\infty} \frac{10^{-x} [Na^+]}{10^{-x} [Na^+] + \varphi(pH)} f^*(x) dx, \quad (15)$$

where $x = pK_c$, $f^*(x)$ is the differential function of the RC distribution in equilibrium constants K_c .

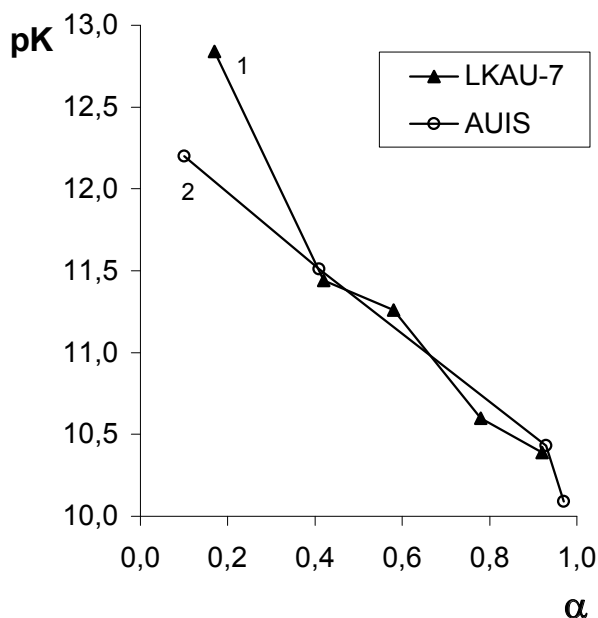


Fig. 3. Dependence $pK = f(\alpha)$. 1 – LKAU-7; 2 – AUIS

In an approximation that $[Na^+] \approx 1$ and $\gamma(Na^+)/\gamma(H^+) \approx 1$, the following expression takes place for DEL model:

$$E = f(pH) = \int_{-\infty}^{+\infty} \frac{10^{-x_T}}{10^{-x_T} + 10^{-pH}} f_T^*(x_T) dx_T, \quad (16)$$

where $x_T = pK_T$, $f_T^*(x_T)$ is the differential function of distribution in thermodynamic constants K_T .

According to Roginskiy's approximation:

$$\left(\frac{dE(pH)}{dpH} \right)_{pH=x_T} \cong f_T^*(x_T), \quad (17)$$

when the coordinates are replaced ($pH = x_T$), the differential potentiogram is transformed into the curve of differential distribution function, and the integral potentiogram, in turn, is transformed to the integral distribution function:

$$(E(pH))_{pH=x_T} \approx \Phi_T^*(x_T), \quad (18)$$

where

$$\Phi_T^*(x_T) = \int_{-\infty}^{+\infty} f_T^*(x_T) dx_T. \quad (19)$$

Gibbs energy for an inhomogeneous sorbent is calculated from the following formula:

$$\Delta G_T^0 = (2.3RT \int_{-\infty}^{+\infty} x_T f_T^*(x_T) dx_T) / E_\infty. \quad (20)$$

This formula is an integral analog of the equation (14).

Since

$$\begin{aligned} \int_{-\infty}^{+\infty} x_T f_T^*(x_T) dx_T &= \\ &= x_T \Phi_T^*(x_T) \Big|_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty} \Phi_T^*(x_T) dx_T, \end{aligned} \quad (21)$$

the following equation is derived using expressions (18), (20) and (21):

$$\Delta G_T^0 \approx 2.3 \frac{RT}{E_\infty} \left(pH_\infty E_\infty - \int_{pH_0}^{pH_\infty} E(pH) dpH \right) \quad (22)$$

where E_∞ is saturation exchange capacity of the sorbent, mmol/g;

pH_∞ is saturation pH value;

pH_0 is the point of zero capacity ($E(pH_0) \approx 0$).

Gibbs energy values of neutralization, calculated at $T = 298$ K according to the formulas (14) and (22), i.e. by MPE and RA methods, are satisfactorily in agreement with each other (Table 2), and account for about (40–50) kJ/mol for different sorbents (i.e. Na^+ -form of the carbon

Table 3. Supposed composition of native analogs of carbon adsorbents*

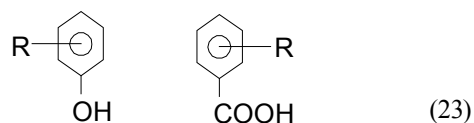
Trade name	Chemical formula			a
	$(x_{ij})_{aq}$ value			
BAU	 9.45	 8.30	 2.87	0.91
LKAU-2	 10.27	 8.00	 4.50	1.17
LKAU-7	 12.56; 9.96	 8.0	 4.41	0.95
AUIS	 4.10	 8.00		1.00

* pK_{T_i} values for RC of i type on a surface of sorbent, calculated in accordance with DEL model, were taken for comparison

adsorbents is thermodynamically unstable). It should be noted that ΔG_{298}^0 values obtained are apparent values and give estimation from below for the true values of Gibbs energy, since the presence of RC, neutralized at $\text{pH} > 12$ on the surface of the sorbent is not excluded.

It is known [14] that the reaction centers, existing on carbon adsorbent surface, are protolytes and they can be viewed as phenolic and carboxylic functional groups localized on a system of condensed aromatic rings (the presence of aldehyde or ether groups on a surface is also

possible). That is why we assume that the nature of RC can be elucidated by comparison of acid-base equilibrium constants for the reaction centers of sorbent and for organic acids (native analogs) in aqueous solution. These acids have the following composition:



where R is $-\text{H}$, $-\text{CH}_3$, $-\text{OCH}_3$, $-\text{OH}$, $-\text{COOH}$, $-\text{COH}$

We compared the pK values in accordance with a hypothesis of free energy linear relation observance [15], i.e. existence of linear correlation between logarithms of protolytic equilibrium constants on a sorbent surface (pK_s) and in aqueous solution (pK_{aq}).

If

$$pK_s = a(pK)_{aq} + b \quad (24)$$

where a and b are constants for the given sorbent, the following relation is satisfied for combination of three indexes of equilibrium constants (x_1, x_2, x_3):

$$\left(\frac{x_3 - x_2}{x_2 - x_1} \right)_s = \left(\frac{x_3 - x_2}{x_2 - x_1} \right)_{aq} \quad (25)$$

The expression (25) and

$$\left(\frac{x_4 - x_3}{x_3 - x_2} \right)_s = \left(\frac{x_4 - x_3}{x_3 - x_2} \right)_{aq} \quad (26)$$

are satisfied for the combination of four indexes of equilibrium constants, and so on.

The search for combinations was carried out as follows. Any two values of $pK_{aq} : (x_i, x_j)_{aq}$ were arbitrarily chosen from a table of acid constants of organic compounds [16] with compositions (23). The other values were calculated using relations (25) and (26) and were compared with table data. We have considered only those variants where the discordance with table data was not more than 0.1 logarithmic units.

The structures of native analogs are given in Table 3. The acid constants of compounds corresponding to (23) are comparable with values obtained for reaction centers of a surface of a sorbent according to the hypothesis of free energy linear relation. This can be considered as an indirect confirmation of the assumption [14], that carboxylic and phenolic groups are the reaction centers of carbon adsorbents.

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