

Adsorption of polyacrylamide on activated carbon

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The adsorption behavior of polyacrylamide (PAA) with different molecular weights ($\overline{M}_n = 5\ 000 - 1\ 350\ 000\ \text{g mol}^{-1}$) on activated carbon (AC) (0.05 – 2.0 g), from aqueous solutions of $0.5\ \text{mol dm}^{-3}\ \text{H}_2\text{SO}_4$, was studied. An effort was made to find a dependence of the quantity of adsorbed PAA, m_a^m (mol g^{-1} or mg g^{-1}), on the polymer equilibrium concentration in the solution, as well as on the molecular weight of the polymer. The viscosimetric study of PAA adsorption on activated carbon from $0.5\ \text{mol dm}^{-3}\ \text{H}_2\text{SO}_4$ at room temperature shows a typical Langmuir behavior following the relation: $m_a^m = 70.6 \cdot \overline{M}_n^{-1.38}$ (mol g^{-1}), where m_a^m is the monomolecular capacity.

Keywords: Adsorption, polyacrylamide, activated carbon, Langmuir isotherm, viscosimetry.

INTRODUCTION

Adsorption of polymers onto solid surfaces has attracted big attention, regarding its practical importance in many areas of application, such as: processes of corrosion inhibition [1-3], mechanical and thermal processing of metals and alloys, surface finish in metal processing, improvement of energy efficiency in fluids transportation, stabilization of colloidal suspensions, preparation of paints, coatings, printing inks, but also in biology, medicine and pharmacology [2, 4].

The features of the polymer/substrate boundary mainly depend on the properties of solid surfaces, type of the solvents used, but in the large extent, on the polymer characteristics, especially the possible changes of the polymer chains conformation in a process of adsorption [5].

Some of the studies of the adsorption behavior of polyacrylamide (PAA) on gold and mild steel from sulfuric and hydrochloric acid, applying cyclic voltammetry, indicated a strong dependence of the adsorption process on polymer molecular weight, electrode potential, as well as temperature [6].

Frumkin's isotherm has been shown to be the best fit to the experimentally obtained values. It has been noticed that, at very low polymer concentration in the solution, polymer adsorption occurs as a result of direct attachment of polymer segments to a metal surface, leading to an almost complete coverage, creating an average thickness of

the adsorbed layer of around 0.8 nm, and a flat orientation of polymer molecules [6].

As far as the electrode potential is concerned, an endothermic process of adsorption of PAA on gold substrate occurs at high anodic potentials, including a simultaneous process of desorption of water molecules and adsorption of PAA macromolecules [6].

Analysis of the effect of temperature on the adsorption mechanism of PAA on silica proposed a decrease of the polymer adsorption on the solid surface, as far as the temperature of the system rises from 15° to $35^\circ\ \text{C}$. Namely, increased temperature leads to conformational changes of the polymer coils into linear forms, disrupting their attachment to solid substrates [7].

Adsorption of polymers has been studied using pure metallic [8, 9] or metal oxide substrates [10, 11]. However, adsorbents based on activated carbon, which is an inert solid material with high porosity and large surface area, attract big attention.

Adsorption of pollutants includes surface interactions between contaminants and activated carbon surfaces *via* van der Waals forces and induced dipole interactions.

Adsorption capacity of activated carbon depends on the size of the inner surface, as well as on the shape and distribution of pore size [12, 13]. Compared to larger carbon particles, μm -sized activated carbon particles enable faster reaction and a greater capacity of contaminant removal. In

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addition to this, modification of surface chemistry has been considered as a convenient technique for improvement of the adsorption capacity of activated carbon [13-16]. Characteristics such as: type, quantity, and concentration of oxygen-containing functional groups, have been considered as crucial in determination of surface features of activated carbon [15].

The aim of this study is to find a correlation between molecular characteristics of polyacrylamide and its adsorption behavior on solid adsorbents, mainly, activated carbon substrate. The adsorption parameters for the best fit of the experimentally obtained data were determined.

EXPERIMENTAL

The adsorption process of polyacrylamide (PAA), with different molecular weights, ($\overline{M}_n = 5\ 000 - 1\ 350\ 000\ \text{g mol}^{-1}$), onto activated carbon (AC) (Merck, p.a. art. 2186) used as adsorbent, from $0.5\ \text{mol dm}^{-3}$ solutions of H_2SO_4 , at a temperature of 293 K, was studied using viscosimetry. Different quantities of activated carbon, from 0.05 to 2 g, were added to $100\ \text{cm}^3$ of $0.5\ \text{mol dm}^{-3}$ aqueous solution of H_2SO_4 , with constant concentration of polymer, 50 - 150 mg ($100\ \text{cm}^3$)⁻¹ with a given molecular weight.

After intensive stirring for at least 6 h, when equilibrium was attained, the suspension was filtered and the equilibrium concentration of PAA in solution was determined viscosimetrically.

The specific surface area of activated carbon was determined by the adsorption of methylene blue from aqueous solution, whose equilibrium concentration was found spectrophotometrically ($\lambda=570\ \text{nm}$).

RESULTS AND DISCUSSION

The previous studies of the adsorption of polyacrylamide (PAA) on gold surfaces, by simultaneous monitoring of the double-layer capacity using cyclic voltammetry, showed that the coverage (θ) of the metal surface with polymer molecules depends on the molar concentration of PAA, as well as on its molecular weight, and the size of the statistical polymer coil in the solution ($R_G = 7.49 \cdot 10^{-3} \cdot \overline{M}_n^{0.64}$) [17]. The results related to the adsorption of PAA on activated carbon, presented in this study, would indicate dependences of the quantity of adsorbed polymer on its equilibrium concentration in the solution and its molecular weight.

The specific area of activated carbon was determined by adsorption of a relatively big organic molecule, such as methylene blue (MB), with a known value of molecule area σ [18, 19] that can only enter in mesopores and larger micropores of the substrate [19, 20]. It is known that the dimensions of methylene blue molecule are $1.43\ \text{nm} \times 0.61\ \text{nm} \times 0.4\ \text{nm}$ [21], thus, each adsorbed molecule of methylene blue takes $0.9\ \text{nm}^2$ of the adsorbent surface.

Equilibrium concentration of methylene blue on activated carbon from aqueous suspensions of AC (20 to 200 mg in $100\ \text{cm}^3$ solution), containing $10^{-3}\ \text{mol dm}^{-3}$ of methylene blue, has been determined by spectrophotometry at $\lambda=570\ \text{nm}$. These results are presented in Table 1 and Fig. 1.

Table 1. Experimental data of methylene blue adsorption ($319.5\ \text{g mol}^{-1}$) on activated carbon from aqueous solutions at 293 K.

C_{AJ} mg ($100\ \text{cm}^3$) ⁻¹	$C \cdot 10^4$ mol dm^{-3}	$m_a^* \cdot 10^5$ mol	$m_a \cdot 10^4$ mol g^{-1}
0	10.0	0	0
20	7.78	2.215	11.07
40	6.34	3.66	9.149
60	4.43	5.57	9.28
80	3.69	7.314	9.143
100	1.47	8.53	8.53
120	0.86	9.14	7.62
160	0.255	9.79	6.094
200	0.202	9.80	4.90

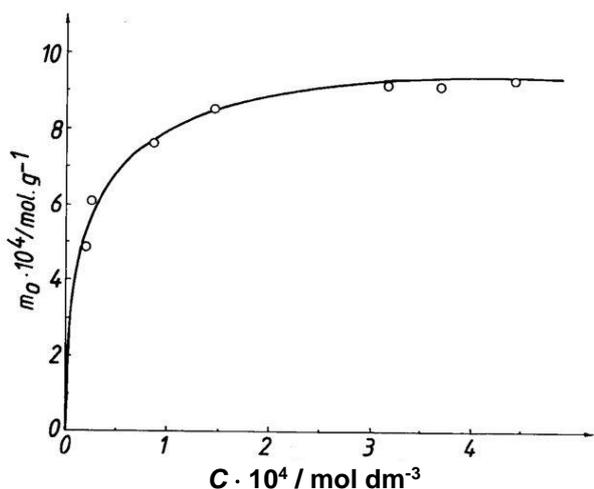


Figure 1. Dependence of the quantity of adsorbed methylene blue on activated carbon on the equilibrium concentration of methylene blue in the solution.

Experimental data show a typical Langmuir behavior of the chemisorption of methylene blue on activated carbon and formation of a monolayer of adsorbed molecules. Monomolecular capacity, m_a^m (mol g⁻¹), as well as adsorption coefficient K_L , were determined using experimental data (Table 1) and Langmuir equation:

$$C/m_a = 1/K_L \cdot m_a^m + C/m_a^m \quad (1)$$

where, C is the equilibrium concentration of methylene blue after adsorption (mol dm⁻³), m_a is adsorbed quantity of methylene blue (mol g⁻¹), K_L is adsorption coefficient (dm³ mol⁻¹), and m_a^m (mol g⁻¹) is monomolecular capacity ($\theta = 1$).

Very good linear relationship was determined by regression analysis of the experimental data (C/m_a)/ C ($R \geq 0.99$), while calculated monomolecular capacity, m_a^m , and adsorption coefficient, K_L , took values of $1.06 \cdot 10^{-3}$ mol g⁻¹ and $2.54 \cdot 10^4$ mol⁻¹ ($\Delta G^\circ = 35.08$ kJ mol⁻¹), respectively. The specific area of activated carbon, 575 m² g⁻¹, was calculated using the equation:

$$A_{AC} = m_a^m \cdot N_A \cdot \sigma_{MB} \cdot 1 \cdot 10^{-18}, \text{ m}^2 \text{ g}^{-1} \quad (2)$$

According to the general pores' classification, micropores in activated carbon are characterized by diameters, d_p , of maximum 2 nm, diameters of mesopores are ranged between 2 and 50 nm, while sizes of macropores are bigger than 50 nm in diameter [22].

As far as the adsorption of PAA is concerned, the dimensions of polyacrylamide coil, given in Table 2, designate that undeformed polymer coil with number average molecular weight $\bar{M}_n = 200$

000 g mol⁻¹ enters into part of the mesopores, $d_p > 40$ nm, and coils with $\bar{M}_n = 600\,000$ and $1\,350\,000$ g mol⁻¹ penetrate just in the macropores of activated carbon. So, the determination of the area of adsorbed macromolecule, σ_{PAA} , requires awareness of the pore distribution in wide ranges, from $d_p = 1$ to $d_p = 200$ nm.

Adsorption of PAA on activated carbon from 0.5 mol dm⁻³ H₂SO₄ was studied viscosimetrically, at a temperature of 293 K. Adsorbent quantities from 0.05 to 2 g were added to 100 cm³ of an aqueous solution of 0.5 M H₂SO₄, and a constant concentration of polymer with a given molecular weight (Table 3).

After rigorous mixing for at least 6 h, the suspension was filtered, and the polymer concentration remaining in the solution was defined by viscosity measurements.

It is known that for a specified solvent at a constant temperature, the viscosity of dilute polymer solutions depends on the polymer concentration in the solution, and its molecular weight. The relationship between intrinsic viscosity and polymer molecular weight is presented by the Mark-Houwink equation, Eqn. 3 [23]:

$$[\eta] = k \bar{M}_n^\alpha \quad (3)$$

where for very dilute solutions:

$$[\eta] = 1/C [2(\eta_{sp} - \ln \eta_{rel})]^{1/2} \quad (4)$$

$$\eta_{sp} = \eta_{rel} - 1 = t/t_0 - 1 \quad (5)$$

Constants k and α depend on the nature of both, solvents and polymers, and also on the temperature.

Viscosimetry measurements of PAA solutions, in 0.5 mol dm⁻³ H₂SO₄, showed linear dependences of viscosity on polymer concentration, Eqns. 6-9 and Fig. 2.

$$\eta_{rel} = 1.902 \cdot 10^{-4} \cdot C + 1.00434 \quad (6)$$

(for $\bar{M}_n = 5\,000$ g mol⁻¹)

$$\eta_{rel} = 2.302 \cdot 10^{-3} \cdot C + 1.00136 \quad (7)$$

(for $\bar{M}_n = 200\,000$ g mol⁻¹)

$$\eta_{rel} = 4.544 \cdot 10^{-3} \cdot C + 0.9812 \quad (8)$$

(for $\bar{M}_n = 600\,000$ g mol⁻¹)

$$\eta_{rel} = 5.434 \cdot 10^{-3} \cdot C + 0.9893 \quad (9)$$

(for $\bar{M}_n = 1\,350\,000$ g mol⁻¹)

These relations clearly indicate that the specific viscosity for dilute polymer solutions in 0.5 mol dm⁻³ H₂SO₄ follows the equation:

$$\eta_{sp} = k \cdot C \quad (10)$$

where the regression analyses directed to the relationship between the constant, k , and polymer's

molecular weight:

$$k = 1.106 \cdot 10^{-6} \cdot \bar{M}_n^{0.623} \quad (11)$$

Table 2. Basic parameters for the size of the statistical polymer coil depending on the molecular weight of PAA.

\bar{M}_n g mol ⁻¹	R_G nm	σ nm ²	$C_s (\theta=1)$ mol m ⁻²	$C_s (\theta=1)$ mg m ⁻²
5 000	1.75	9.6	$1.74 \cdot 10^{-7}$	0.870
200 000	18.50	1075	$1.55 \cdot 10^{-9}$	0.300
600 000	37.40	4385.7	$3.78 \cdot 10^{-10}$	0.227
1 350 000	62.80	12 383	$1.34 \cdot 10^{-10}$	0.181

Table 3. Experimental data of PAA adsorption on activated carbon from aqueous solutions of 0.5 mol dm⁻³ H₂SO₄, obtained viscosimetrically.

\bar{M}_n^{PAA} g mol ⁻¹	C^{PAA} mol dm ⁻³	C_{AJ} mg(100 cm ³) ⁻¹	η_{rel} ($t = 6\text{h}$)	m_a^{PAA} mg (100 cm ³) ⁻¹	$C_e^{\text{PAA}} \cdot 10^6$ mol dm ⁻³	$m_a \cdot 10^6$ mol g ⁻¹
200 000	$7.5 \cdot 10^{-6}$ [150 mg(100 cm ³) ⁻¹]	0	1.3467	150	7.50	0.000
		40	1.289	125	6.25	3.125
		50	1.271	117	5.85	3.300
		80	1.222	96	4.80	3.375
		180	1.0796	34	1.685	3.222
		300	1.0543	23	1.145	2.120
		500	1.0416	17.5	0.875	1.325
600 000	$1.67 \cdot 10^{-6}$ [100 mg(100 cm ³) ⁻¹]	700	1.0382	16	0.820	0.957
		0	1.4353	100	1.670	0.000
		60	1.3195	74.5	1.244	0.708
		90	1.2537	60	1.002	0.741
		160	1.0990	26	0.434	0.771
		250	1.0312	11	0.184	0.593
1 350 000	$3.7 \cdot 10^{-7}$ [50 mg(100 cm ³) ⁻¹]	500	1.0085	~6	0.100	0.313
		0	1.2611	50	0.370	0.000
		30	1.2067	~40	0.296	0.247
		50	1.1741	34	0.252	0.237
		80	1.1252	25	0.185	0.185
		180	1.049	11	0.082	0.161
300	1.014	~4.5	0.033	0.112		
500	1.011	~4.0	0.0296	0.068		

Table 4. Thermodynamic parameters for adsorption of PAA on activated carbon from aqueous solutions of 0.5 mol dm⁻³ H₂SO₄, at 293 K.

\bar{M}_n^{PAA} g mol ⁻¹	m_a^m mol g ⁻¹ (mg g ⁻¹)	K_L dm ³ mol ⁻¹	$-\Delta G^0$ kJ mol ⁻¹
5 000	$3.854 \cdot 10^{-5}$ (~193)	$5.575 \cdot 10^4$	36.41
200 000	$3.48 \cdot 10^{-6}$ (696)	$2.45 \cdot 10^6$	45.62
600 000	$7.755 \cdot 10^{-7}$ (465)	$1.343 \cdot 10^7$	49.77
1 350 000	$2.523 \cdot 10^{-7}$ (340)	$3.668 \cdot 10^7$	52.21
Methylene blue (319.5)	$1.06 \cdot 10^{-3}$ (339)	$2.54 \cdot 10^4$	35.08

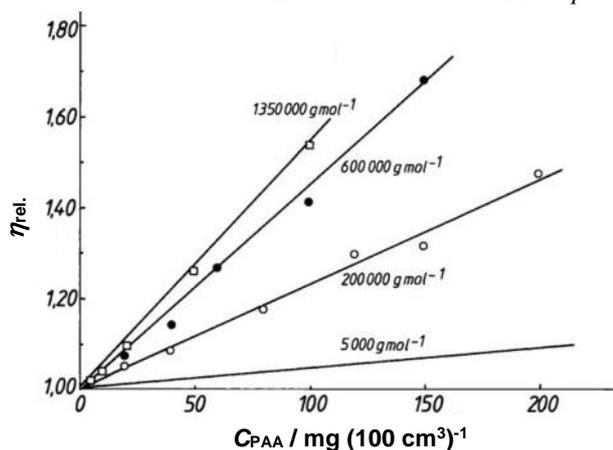


Figure 2. Dependences of relative viscosity on PAA concentration in aqueous solution of $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ at 293 K.

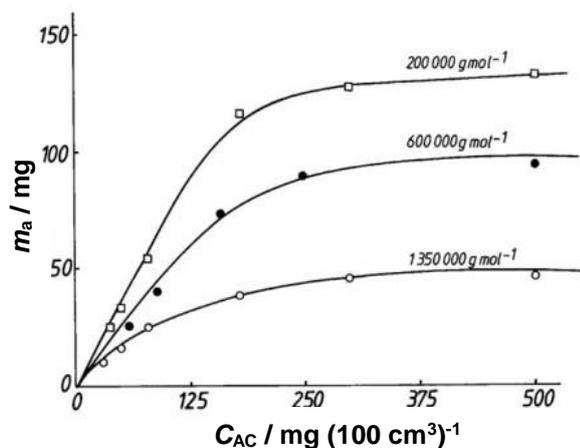


Figure 3. Dependences of adsorbed PAA quantity on AC concentration in 0.5 mol dm^{-3} aqueous solution of H_2SO_4 at 293 K.

Thus,

$$\eta_{sp} / C = 1.106 \cdot 10^{-6} \cdot \bar{M}_n^{0.623} \quad (12)$$

where C is the PAA concentration in the solution ($\text{mg} / 100 \text{ cm}^3$ solution).

Direct correlation of the hydrodynamic volume of the polymer coil ($4/3R_G^3\pi$) on polymer viscosity and molecular weight is given by Eqn. 13 [24]:

$$v = 100 [\eta] M / N_A = 4/3 R_G^3\pi \quad (13)$$

where, R_G is the radius of giration (cm), M is molecular weight of the polymer (g mol^{-1}), and $[\eta]$ is characteristic viscosity of polymer solution.

Dependences of adsorbed quantity of PAA on the concentration of activated carbon for different molecular weights are given in Figure 3.

Equilibrium concentration of PAA in the solution, i.e., adsorbed polymer quantity on activated carbon, was calculated using experimental data of the relative viscosity of the filtrate.

Experimentally obtained values, Table 3, were fitted to the Langmuir equation, and the values of the basic adsorption parameters are presented in Table 4.

Adsorption coefficient, K_L , as well as Gibbs energy of adsorption process, clearly depend on PAA molecular weight, as it was previously shown for PAA adsorption on gold substrates [17].

It is obvious that an increase in polymer molecular weight influences a decrease of the monomolecular capacity of the adsorbed polymer, which is in accordance with the results related to the adsorption of poly(methyl methacrylate) on carbon black or Al_2O_3 [24].

The relations of the monomolecular adsorption capacity, m_a^m , on the molecular weight are presented by Eqn. 14:

$$m_a^m = k \cdot \bar{M}_n^\alpha \quad (14)$$

So that:

$$m_a^m = 70.6 \cdot \bar{M}_n^{-1.38} \quad (\text{mol g}^{-1}) \quad (15)$$

or

$$m_a^m = 7.04 \cdot 10^4 \cdot \bar{M}_n^{-0.382} \quad (\text{mg g}^{-1}) \quad (16)$$

Similar relations were determined for the adsorption model of undistorted polymer coil on a solid surface (Table 2):

$$m_a^m = 9.47 \cdot 10^{-3} \cdot \bar{M}_n^{-1.28} \quad (\text{mol m}^{-2}) \quad (17)$$

or

$$m_a^m = 9.43 \cdot \bar{M}_n^{-0.28} \quad (\text{mg m}^{-2}) \quad (18)$$

Experimentally obtained data for monomolecular capacity, m_a^m (mg g^{-1} , Table 4), as well as those for C_s (mg m^{-2} , Table 2), indicate a significant deformation of the polymer coil during the process of adsorption on activated carbon.

CONCLUSIONS

The adsorption process of polyacrylamide (PAA) with different molecular weights ($\bar{M}_n = 5\,000 - 1\,350\,000 \text{ g mol}^{-1}$) on activated carbon, studied by viscosimetry, showed a typical Langmuir behavior. A clear dependence of the monomolecular capacity of PAA on the polymer molecular weight, $m_a^m = 70.6 \cdot \bar{M}_n^{-1.38} \text{ (mol g}^{-1}\text{)}$, was shown. The comparison of this equation with the relation $m_a^m = k \cdot \bar{M}_n^{-1.38}$, obtained for undistorted polymer coil, indicates a significant deformation of PAA at the time of the adsorption process on activated carbon.

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