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Interactions of xanthines with activated carbon
II. The adsorption equilibrium

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Abstract

In the present work, we have studied the adsorption of xanthine derivatives by activated carbon sorbents in aqueous solutions. The study comprised both kinetic, equilibrium and thermodynamic aspects. The kinetic results were reported in a previous paper; the equilibrium-related results are discussed here. The two types of carbon used exhibit some differences but the equilibrium isotherms obtained are all of the H-3 type in the classification of Giles. This suggests a high affinity of the sorbents for the sorbates. We also found that the overall adsorption process comprises more than one individual adsorption–desorption process of which one leads to the formation of a ''monolayer'' and the other to the ''precipitation'' of the sorbate on the sorbent surface (multilayer adsorption); the amount of sorbate adsorbed in monolayer form was seemingly greater in C-A14.

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1. Introduction

As stated in a previous paper [1], some xanthine derivatives exhibit pharmacological action and are used as coagents for β-adrenergics and corticoids in the treatment of asthma, bronchitis and emphysema. Such derivatives are usually purified by adsorption of their water-soluble impurities in activated carbon, a process that is also highly useful for treating potential poisoning by these substances [2].

The foregoing, and the fact that a xanthine derivative has been used as a selective sorbate for determining the total surface area of activated carbon [3], led us to study the adsorption of xanthine derivatives by activated carbon sorbents in aqueous solutions. The study comprised both kinetic, equilibrium and thermodynamic aspects. The kinetic results were reported in a previous paper [1]; the equilibrium-related results are discussed here.

The adsorption isotherms of sorbates by solids in dissolution may present different shapes, as can be appreciated in the classification proposed by Giles et al. [4,5]. The individual adsorption isotherm is source of information about both, the solid surface and the interaction process (active sites) with the sorbate. To obtain it, we have to fit the experimental results to the mathematical equation corresponding to a before postulated model. These equations are (oftenly) gases adsorption isotherms, suitably transformed, as them proposed by Henry [6], Freundlich [7], Langmuir [8], Zhukovitsky or that of Dahms and Green [9,10], Frumkin [11,12], Bockris [13], Brunauer [14,15], Tiren [16], Jowet [17], Temkin [18,19] and Derylo-Jaroniec [20].

The Derylo-Jaroniec integrated equation was proposed to describe the overall gas adsorption process by an energetically homogeneous solid, using as point of item different local adsorption isotherms that lead to integral equations, which should describe the global adsorption isotherm.

One of these equations, frequently used in the last years, is that of Tóht. The equation called of Tóth (or more exactly of Marczewski and Jaroniec), has reached a considerable acceptance. Later, Dabrowski, Jaroniec and Tóth [21]

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modificated it with the goal of adapting it to the needs that appear on studying the adsorption isotherms by solids in dissolution, and proposed a semiempirical one known like ‘‘Tóht-modified Equation’’ [21].

In the present work, we postulate that the experimental isotherms are the result of the sum of the individual ones corresponding to two or more simple reversible adsorption–desorption processes and, in its case, to one sorbate condensation or precipitation process. All the isotherms of the already cited Giles's classification are satisfactory fitted to the following equation [22]:

$$\theta = \frac{n^{\mathrm{s}}}{n^{\mathrm{s}}_{\mathrm{m}}} = \sum_{i=1}^{i=j} \frac{K_i C_i^n}{1 + K_i C_i^n} + K_f C^m \qquad (1)$$

2. Experimental

The sorbents used were a commercially available product (Merck ref. 2514), henceforth, referred to as C-M and one prepared in our laboratory that was designated C-A14 [1]. Both were used in particle sizes over the range 0.50–0.59 mm and characterized by using appropriate methods described elsewhere [1].

The aqueous sorbates used included caffeine (CF), theophylline (TP), theobromine (TB), 1,3,8-trimethylxanthine (TM) and 1,3-dimethyl-8-ethylxanthine (ET). Their concentrations in solution were determined by UV spectrophotometry [23,24].

Adsorption isotherms were obtained as described in a previous paper [1], using 100 ml of a 10^{-3} M solution of each sorbate and known amounts of sorbent from 0.030 to 0.900 g. The solid phase and the solution were kept in contact at a constant temperature of 10, 20, 30, 40 or 50 °C for much longer than needed to reach equilibrium. Equilibration times ranged from 150 to 2300 h, depending on the particular sorbent—they were invariably shorter for C-M—and temperature—they decreased with increasing *T*.

In order to obtain accurate equilibrium isotherms, we initially used near-saturated solutions; this allowed equilibrium concentrations between the lowest analytically detectable level and a value close to the initial one to be obtained. Because the solubility values for some sorbates at specific temperatures were unavailable, we determined their water solubility at each studied temperature.

3. Results and discussion

Table 1
Water solubility of the xanthines

	$C_s \times 10^3$ (mol/L)				
	CF	TF	TB	TM	ET
T (°C)					
10	52.2	17.7	1.33	8.05	8.27
20	89.4	28.4	2.08	13.9	10.1
30	137	44.9	3.08	22.1	12.8
40	235	73.9	4.65	31.7	16.0
50	373	111	6.65	40.2	20.1
ΔH_s (kJ/mol)	37.0	35.2	30.6	36.5	16.9
ΔS_s (J/K mol)	107	91.2	53.5	89.8	20.4

Table 1 shows the solubility data (C_s) obtained alongside the ΔH_s and ΔS_s values for the dissolution process, which were determined from ln C_s versus 1/*T* plots. We checked our values against their reported counterparts where available (e.g. for caffeine [25,26]). Also, we found the ln C_s versus 1/*T* plot for TM to consist of two straight segments with an apparent inflection at ca. 30 °C; this suggests that, depending on the particular concentration and temperature, the initial solute (the monomer) underwent substantial changes (dimerization or oligomerization) as previously found in caffeine by Lilley [25]. According to this author, the overall process by which caffeine is dissolved in water comprises two individual processes, namely: dissolution proper, with $\Delta H_1 = 20.9$ kJ/mol, and dimerization of the solute, with $\Delta H_2 = 14.2$ kJ/mol. Based on our solubility data, the enthalpy changes for these steps in TM dissolution would be $\Delta H_1 = 23.7$ kJ/mol and $\Delta H_2 = 12.8$ kJ/mol, and their combined value 36.5 kJ/mol—the datum listed in Table 1. The fact that ln C_s versus 1/*T* plots (for the other xanthine derivatives) exhibited no inflection points, probably indicate that both individual processes cannot be separated depending on temperature, inside the studied interval.

The equilibrium results for the studied processes were expressed as moles (n^s) of sorbate adsorbed per gram of sorbent at an absolute (C) or relative (C/C_0) equilibrium concentration and were plotted as a function of C/C_0. Fig. 1 shows a selected plot. While the two types of carbon exhibited some differences, the equilibrium isotherms were all of the H-3 type in the classification of Giles [4]. This suggests a high affinity of the sorbents for the sorbates.

The presence of a more or less well-defined rising portion at the highest equilibrium concentrations is suggestive of multilayer adsorption. This, in turn, suggests that the overall adsorption process comprises one or more individual adsorption–desorption steps of which one leads to the formation of a ‘‘monolayer’’ and the other to the ‘‘precipitation’’ of the sorbate on the sorbent surface (multilayer adsorption). The amount of sorbate adsorbed in monolayer form was seemingly greater in

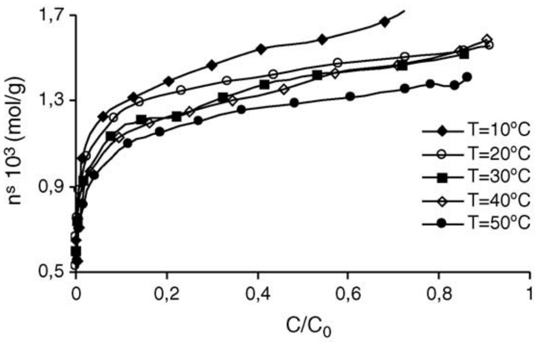

Fig. 1. Isotherms for the retention of CF by the Merck carbon in an aqueous solution.