

## Theoretical and experimental peculiarities of adsorption from solutions

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**Abstract:**—The interrelation between the state of solute and its adsorption on porous polymer adsorbents, taking as an example the dye adsorption on cellulose, is considered. The validity of the theory of micropores volume filling and the possibility of calculating the adsorption parameters on its basis is substantiated. The controversial matter of analogy of the adsorption process with the volumetric dissolving is discussed.

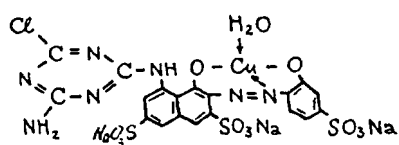
### Introduction

The phenomenon of adsorption from solutions on the surface of solid adsorbents is a basis of numerous physico-chemical and biochemical processes. For a long time the interest to this phenomenon was determined by the necessity of solving purely applied problems (dyeing, catalysis, sewage purification and so forth). Recently the considerable progress has been observed in the development theory of the adsorption from solutions. However, the solution of many fundamental problems is far from completion. The purpose of this investigation is to find out some quantitative regularities of the solution properties effect on the adsorption of dissolved substances on porous polymer adsorbents.

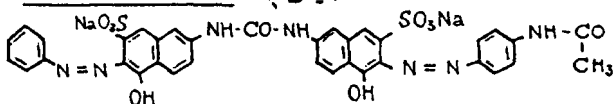
### Properties of dye solutions

Depending on the nature of dye (Fig.1) and solvent, dye can be in the form of various intercomplex compounds, separate molecules, ions and associates, which coexist in dynamic equilibrium.

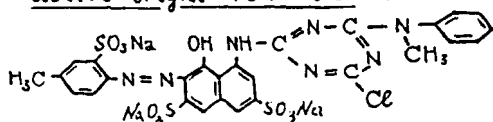
#### active violet 4K (AV-4K)



#### direct scarlet (DS)



#### active bright-red 6C (ABR-6C)



#### acid orange (AO)

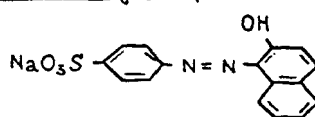


Fig.1. The chemical formulae of the dyes.

Let us consider the peculiarities of the dyes state in solutions and the effect of the mixed solvent composition on the thermodynamic properties of the dyes dissolving (solvation). The most precise determinable thermodynamic values, enabling to judge not only about dissolving but solvation as well, is the solution enthalpy (Fig.2-4).

When comparing the solution enthalpy as a function of concentration for the dyes with mineral electrolytes, attention is attracted by two marked distinctions: in the first place, the absence of the Debye-Huckel region for the low concentration solutions of dye, secondly, the opposite dependencies of  $\Delta_{\text{soln}} H = f(m)$ . At higher concentrations appears the steep increase in exothermic nature of dissolving.

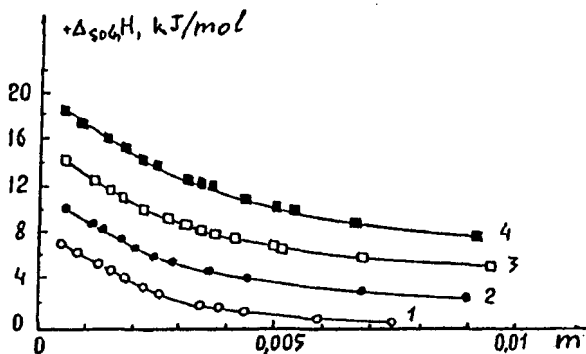


Fig. 2. The concentration and temperature dependence of the solution enthalpy for the AO dye in water (1-298, 2-308, 3-328 K)

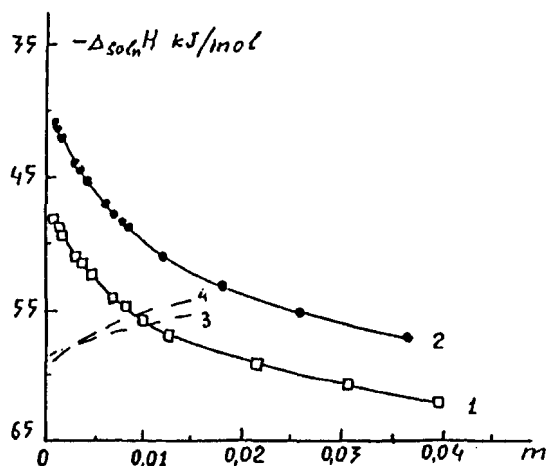


Fig. 3. The concentration dependencies of the solution enthalpy at 298K for AV-4K dye in 2m urea (1) and 0.05m NaCl (2) aqueous solutions; LiCl in water (3); NaI in acetone.

Such concentration dependencies are connected with the predomination of exothermic contribution of the organic ions association over the endothermic effect of dehydration, that is, with the existence of solvate-divided associates, the formation of which is promoted by the presence of inorganic electrolytes and decreasing temperature [2-4]. The investigation of the solution thermodynamics of dyes shows that predominant contribution into  $\Delta_{\text{soln}} G$  is the entropy one. For example, for the acid orange dye at 298K  $\Delta_{\text{soln}} G^{\circ} = 47.9$ ,  $\Delta_{\text{soln}} H^{\circ} = 15.6$ ,  $T\Delta_{\text{soln}} S^{\circ} = -32.3$  (kJ/mol). In connection with the absence of solvation values for the many dyes it makes sense to carry out the discussion of the thermodynamic properties of such solutions on the basis of the thermodynamic properties transfer. According to Fig. 5 the values of  $\Delta_{\text{trf}} H$  from water into water-dimethylformamide (DMFA) and water-dimethylsulfoxide (DMSO) at m.f. organic component more 0.3 monotonically go into more exothermic region. At the same time the changes in the standard enthalpies of the organic ion transfer from water into the mixed solvents are of strongly pronounced extreme character. The material considered enables to draw the following conclusions:

- the formation of dye solutions occurs with considerable and, perhaps, decisive of the Hibbs entropy contribution;
- the existence of different degree of organic ions hydrophility and hydrophobity leads to the fact, that more hydrophobic ones stabilize the solvent structure in greater extent and are more liable to association;
- at the formation of ionogenic dyes solutions in mixed solvents an organic ion behaves like a nonaqueous component of solvent, competing with the latter in the effect on water structure and in the formation of the solute-water bond.

#### Adsorptions process

Before examining the adsorption process it is necessary to characterize the cellulose materials porosity. A major part of micropores volume are due to the pores less than 3 nm in diameter. The analysis of the data, shown in Table 1, enables to suggest that the swelling is accompanied by the structural changes of fiber, causing

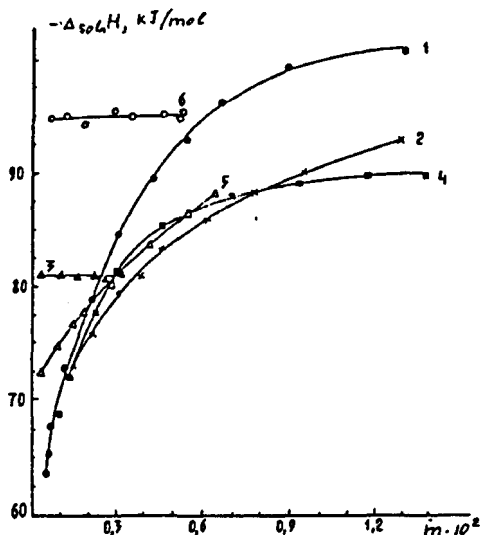


Fig. 4. The concentration dependence of the solution enthalpy for DS dye at 298K in aqueous solutions: 0.01M NaCl (1); 0.1M NaCl (2); 0.4M NaCl (3); 0.01M Na<sub>2</sub>SO<sub>4</sub> (4); 0.05M Na<sub>2</sub>SO<sub>4</sub> (5); 0.1M Na<sub>2</sub>SO<sub>4</sub> (6).

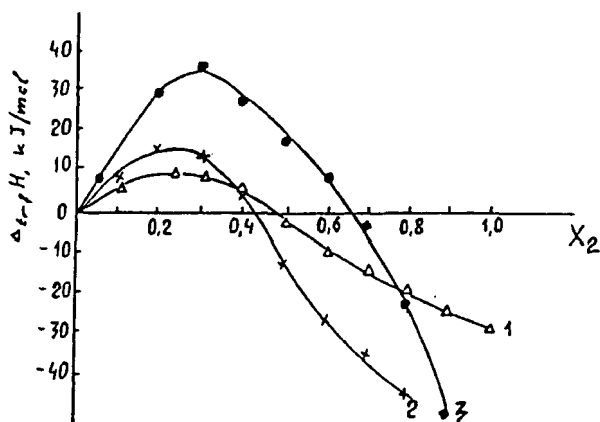


Fig. 5. The standard enthalpies of transfer of chrysophenine (1) and DS (2) dyes from water into DMFA; the one for DS dye transfer (3) from water into water-DMSO.

the formation of meso- and micropores because of the reduction in the number of macropores.

The basic difference between adsorption from solution and gas and vapors adsorption lies in the fact that the first one is displacing in character and occurs by the way of the solution components redistribution over the phases interfaces. Thus, the energetic properties, obtained from the isotherms of adsorption or calorimetry, characterize the difference in the of solute-solvent and solute-adsorbent interaction. Therefore, it is interesting to connect the state of solute in solution (solvation, association) with the state of solution in "adsorption phase".

TABLE 1. The parameters of the cellulose samples porous structure

Materials	Pores volume, sm <sup>3</sup> /g					
	micropores r <sub>eff</sub> < 1.5 nm		mesopores 1.5 nm < r <sub>eff</sub> < 100 nm		macropores r <sub>eff</sub> > 100 nm	
	octan	water	octan	water	octan	water
1	0.03	0.07	0.02	0.26	1.12	0.98
2	0.03	0.11	0.02	0.28	1.00	0.86

To investigate the vapor adsorption on microporous adsorbents Dubinin suggested a theory of micropores volume filling, according to which the fixation of solute molecules in the total field of all the atoms of solid, surrounding the pore cavity, occurs not only in the region of interior pore surface, but also in the volume of interpore space. Numerous experimental investigations of adsorption of different classes of inorganic dyes from aqueous and mixed solvents on cellulose fiber have shown that their adsorption is well described by the equation of the micropores volume filling theory for the concentrations in solution from 10<sup>-6</sup> to saturation. Therefore, our further discussion is based on the micropores volume filling theory. This theory establishes relation between the degree of adsorption space (volume) filling and the differential molar work of adsorption.

According to Serpinsky's works [1], the phenomena of physical adsorption on microporous adsorbents are similar to volumetric dissolving. The thermodynamic basis of adsorption in this case is the Gibbs-Duhem equation. The chemical potential of the adsorbent changes in ion (molecular) adsorption like the chemical potential in solution formation.

In this case one can apply the theory of micropores volume filling according to which the whole volume of the pores adsorption space is the volume of the effective adsorption field. Under these conditions microporous adsorbent is active in physical adsorption. Thermodynamic activeness of microporous adsorbent is bound to lead to the statement that microporous solid and n-component adsorbate, being n phases when considered separately, cease to be ones after adsorption, and forming, as a result, a single (n+1)-component phase.

Fig. 6,7 show the isotherms of adsorption of the AV-4K and ABR-6C dyes from water and water-salt solutions. The experimental data [5,6] has demonstrated that the adsorption on cotton fiber is described by the Dubinin-Astakhov equation.

$$\ln C_f = \ln C_\infty - (RT/E)^n (\ln(c_s/c_1))^n \quad (1)$$

The change of n from 1 for aqueous solution to 2 for water-salt one seems unexpected at first sight (Table 2), as this change is connected with the increase in the adsorption potential, which is determined, essentially, by the size of the adsorbent pores. It is assumed that n is constant and determines the width of the pores distribution function and that the characteristic energy E is equal to the most probable value of the adsorption potential. In this case one can suggest that the introduction of inorganic electrolyte into the dye solution results not only in the change of the chemical potential of dye but also for adsorbent. That leads to the increase of the adsorption potential and in the value of adsorption. The obtained limiting values of adsorption in aqueous and water-salt solutions ( $C_\infty$ ) for the same dye are essentially equal and temperature independent.

Lower values of  $C_\infty$  in the case of the ABR-6C dye are due to the particular dye as more branched and less planar structure. Thus, one of the apparent contradictions of the Langmuir adsorption model - the dependence of the maximum value of dye adsorption on the concentration of inorganic electrolyte - is removed.

TABLE 2. The values of the Dubinin-Astakhov equation parameters for the ABR-6C dye ( $C_\infty$ , mol/kg;  $C_s$ , mol/l;  $RT/E$ , J/mol)

Parameter	298 K		308 K		318 K		328 K	
	1	2	1	2	1	2	1	2
Aqueous solution								
$C_\infty \cdot 10^2$	1.67	1.60						
$RT/E$	0.826	0.826						
$C_s$	0.153	0.145						
Aqueous solution of NaCl (0.1 M) (n=2)								
$C_\infty \cdot 10^2$	1.64	1.62	1.58	1.59	1.60	1.58	1.52	1.51
$(RT/E)^2 \cdot 10^2$	5.74	5.78	5.85	5.82	6.01	5.94	6.38	6.39
$C_s$	0.140	0.135	0.157	0.161	0.138	0.202	0.237	0.234

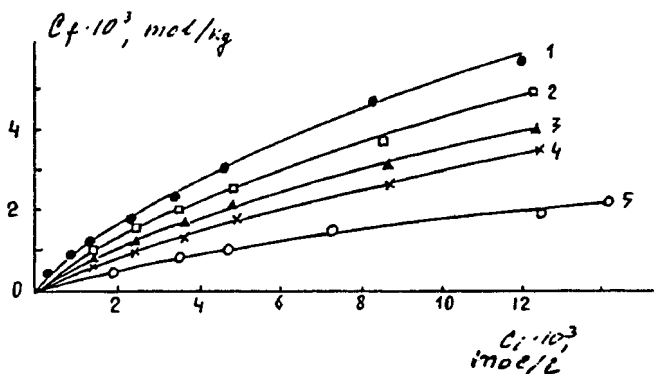


Fig. 6. The adsorption isotherms of the AV-4K dye at 298K (1); 308K (2); 318K (3); 328K (4); and the ABR-6C one at 298K (5) from water solutions.

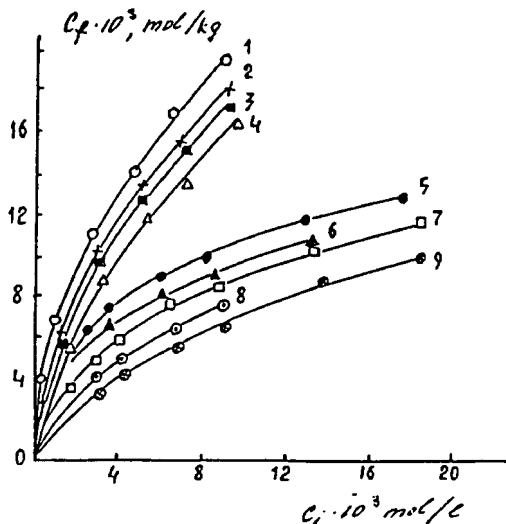


Fig. 7. The adsorption isotherms of the AV-4K dye at 298K (1); 308K (2); 318K (3); 328K (4) and the ABR-6C one at 298K (5); 308K (6); 318K (7); 328K (8); 348K (9) from aqueous solutions of NaCl (0.1 M).

The calculated adsorption volumes of the dyes ( $V_{\infty} = c_{\infty} V^*$ , where  $V^*$  - the molar volume of dye) are listed in the Table 3.

The limiting adsorption volumes, obtained as from water as water-salt solutions, for the violet 4K dye and bright-red 6C one are equal.

To determine  $V_{\infty}$  is limited by the cases when the interaction between dye and solvent is less than that between dye and fiber, but the difference of adsorption energies of both solution components is considerable.

The joint analysis of the solubility data (solubility increases with rising temperature) and the enthalpy of dissolving ( $\Delta_{\text{soln}} H^m$  becomes less exothermic with increasing temperature) with the use of the Gibbs-Gelmgolz equation shows that the enthalpy contribution opposes the process of dye dissolving with rising temperature and the increase in solubility occurs due to the entropy factor.

TABLE 3. The isotherm parameters of the active dyes adsorption from water and 0.1 M NaCl solution on cotton fiber at 298 K

Dye	Solvent	$V_{\infty}$ l/kg	$C_1$ , mol/l at $C_f = 0.368C_{\infty}$	$\ln \frac{\gamma_{\infty}}{\gamma_s}$	$\ln \frac{\gamma_{\infty}}{\gamma_s}$	E J/mol	$-\Delta_{\text{ads}} G^{\circ}$ , J/mol
Violet 4K	Water	0.22	$3.184 \cdot 10^{-2}$	1.29	-	3465	-
	0.1 M NaCl	0.22	$2.69 \cdot 10^{-2}$	3.71	3.69	9504	9458
Bright-red 6C	Water	0.14	$4.56 \cdot 10^{-2}$	1.46	-	3000	-
	0.1 M NaCl	0.14	$2.15 \cdot 10^{-2}$	-	4.36	10340	-

As adsorption is exothermic process the increasing temperature should decrease the value of adsorption. However, considering adsorption from solutions one should take into account the effect of temperature on the solubility of substance that is on the value of its chemical

potential in solution. It is the combination of these two factors that determines the resulting effect of temperature on the equilibrium in adsorption from solutions.

It is generally accepted that the addition of inorganic electrolyte to aqueous solutions of dyes effect the DEL of fiber material and, thus, favors the increase of the solute extraction. However, according to the mentioned above, inorganic electrolyte decreases as well the of interaction of water both with dye and cellulose fiber, that, in its turn, also favors the adsorption process. The change of the dye transfer from bulk to adsorption phase can effect the differential adsorption heats as the weakening of the interaction of water with dye and fiber should lead to the increase of dehydration degree of the latter in adsorption. To prove this suggestion integral adsorption heats of the active violet 4K dye from water and water-salt solutions (Fig. 8) have been measured. One can see that the differential adsorption heats, calculated from calorimetry, and isosteric ones differ.

Generally speaking, the matter of an agreement between calorimetric and isosteric adsorption heats is not so trivial. Such agreement may not exist, if a system displays hysteresis (porous adsorbent) and in the case of heterogeneous surface, such agreement is hard to substantiate thermodynamically. Nevertheless, it is obvious that the adsorption heats decrease both with the increase in the degree of volume filling and with the switch from aqueous solutions to water-salt ones. One should also note that the change of differential heats of adsorption with the increase in the amount of adsorbed dye is opposite to the change in the thermal effect of dissolving.

This leads to the conclusion that the more associated the dye and the higher the ex effect of dissolving the less is the adsorption heat. And as the exoeffect of the adsorption from water-salt solutions is less than that for the adsorption from water and the amount of the adsorbed dye is higher, than, evidently, the role of the entropy factor in the adsorption process increases.

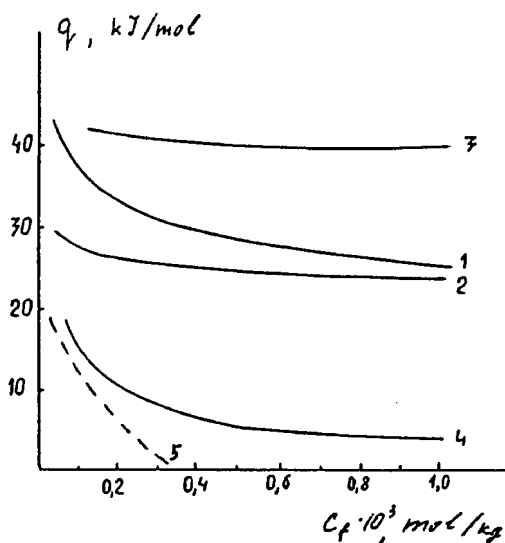


Fig. 8. The differential heats of adsorption of the AV-4K dye at 298K from water (1,3) and 0.1 M NaCl solution (2,4), calculated from the Clausius-Clapeyron equation (1,2) and by the differentiation of the experimental integral heats (3,4), DS at 298K from 0.4M NaCl.

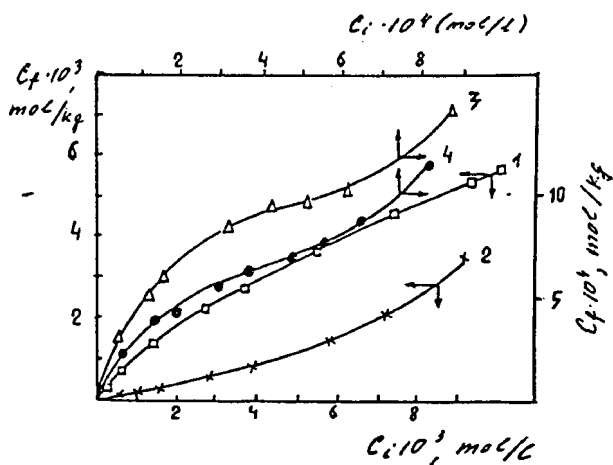


Fig. 9. The adsorption isotherms: 1 - AV-4K from the water-DMSO (0.01 m.f.); 2- AV-4K from water-DMFA (0.1 m.f.) at 298K; 3,4 -DA from the water-DMFA (0.1 m.f.) at 298K and 308K, correspondingly.

At increasing temperature association degree of the organic ions decreases that favors the increase of dye adsorption to the rise in a number of available micropores and the increase in a fraction of the micropores filled with one component of the solute.

The differential adsorption heats of direct scarlet (Fig. 8) from water-salt solution sharply decrease with the rise in the degree of filling (it proves the presence of strongly associated dye in micropores that decrease the sorption heat due to resolution). Increasing temperature induces sharp decrease in differential heats of adsorption. In this connection (as in the case of active dyes) one may say about prevailing effect of the entropy factor on the mass-transfer of dye from solution into fiber. And in the case of dyes, liable to strong association, one should take into account the so called sieve effect— inaccessibility of some part of micropores volume for large associates.

At addition of nonaqueous component (Fig.9) the dye adsorption isotherms change their shape. Such behavior can indicate weak interaction of the dye with adsorbent, the increase in the interaction between the DMSO and adsorbent (DMSO is better solvated by fiber than by water) and also the strengthening of interaction between the adsorbed molecules of the dye.

#### Thermodynamic of adsorption

The analysis of the data indicates that the mechanism of dye adsorption is affected by the structure of dyes, their state in solution, nature and composition of solvent, temperature.

As a result the necessity of establishing the relation between the state of dyes in solution and the thermodynamic properties of adsorption arises.

As has been stated before, the adsorption in micropores is similar to the phenomenon of volumetric dissolving. Let us consider the adsorption equilibrium. The driving force of the adsorption process is the difference in chemical potentials of substrate in bulk and adsorption phases. As the reference state of the solute in solution and "adsorption phase" we take its state in hypothetical ideal solution with  $\gamma=1$ .

The change of solute chemical potential at formation of real solution in bulk and "adsorption phases" can be written as follows:

$$\bar{G} = \bar{G}^0 + RT \ln(a) \quad (2)$$

$$\bar{G}_f^s = \bar{G}_f^0 + RT \ln(a_f^s) \quad (3)$$

At equilibrium

$$\bar{G}_f = \bar{G}_s \quad (4)$$

$$\text{then } \Delta G_{ads}^0 = (\bar{G}_f^0 - \bar{G}_s^0) = -RT(\ln(c_\infty/c_s) + \ln(\gamma_\infty/\gamma_s)) \quad (5)$$

On the other hand, we have an adsorption equilibrium at limiting ( $C_\infty$ ,  $C_s$ ) and real ( $C_f$ ,  $C_s$ ) concentrations. Making some transformations, we obtain:

$$-RT \ln(a_\infty) + RT \ln(a_f) = -RT \ln(a_s) + RT \ln(a_1) \quad (6)$$

Then

$$\ln(\gamma_\infty \gamma_1 / \gamma_f \gamma_s) = \ln(c_s c_f / c_\infty c_1) \quad (7)$$

To find  $\Delta_{ads} G^0$  it is necessary to know  $V_\infty$ ,  $\ln(\gamma_\infty/\gamma_s)$  or  $\ln(\gamma_f/\gamma_1)$ .

Other values can be obtained from the isotherm of adsorption. The function

$$\ln(\gamma_{\infty}\gamma_1/\gamma_f\gamma_s)=f(c_1) \quad (8)$$

has the inflection point. At this point there is a possibility

$$\ln(c_s c_f/c_{\infty} c_1)=\ln(\gamma_{\infty}/\gamma_s) \quad (9)$$

Given the value  $\ln(\gamma_{\infty}/\gamma_s)$ , one can calculate  $\Delta_{ads} G^0$ .

#### Conclusions:

1. The adsorption of organic electrolytes from aqueous solutions on porous adsorbents is well described by the theory of micropores volume filling.

2. It is possible to describe the thermodynamic of adsorption on porous adsorbents considering the similarity of adsorption and volumetric dissolving.

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