The Role of the Entropy Factor on the Adsorption of an Optical Brightener on Pulp

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The present paper reports results of the thermodynamic study of adsorption of 2 optical brighteners (Tinopal UP and Leucophor AP) on pulp. The entropy non-homogeneity of the pulp surface was confirmed and the coefficients of entropy non-homogeneity were determined. The entropy effect on the variation of Gibbs free energy of the process studied was followed.

Key Words: Optical brighteners, pulp, adsorption, entropy non-homogeneity.

Introduction

Optical brighteners (OBs) are widely used in the paper industry to increase the whiteness of paper products. For the paper maker, the usage of OBs is one of the tools to eliminate the yellowish of chemical pulp. OBs convert invisible ultraviolet radiation to visible blue light. The additional light source on the fibre, superimposed on normal light from the paper, gives a very brilliant, neutral white.[1,2]

It is found that the pulp surface is uniformly non-homogeneous with ensembles of identical numbers of active centres with different degrees of adsorption ability.[3−9] The interaction between the pulp and the OBs is an adsorption controlled heterogeneous process. The adsorption proceeds through rupture of hydrogen type bonds between the hydroxyl groups of adjacent chains in the pulp, which results in new adsorption centres. New bonds are formed between the hydrogen of the hydroxyl groups of the pulp and the oxygen or the nitrogen of the polar groups of the brighteners.[10−15]

The adsorption equilibrium between OBs and pulp was studied at degree of surface coverage $\theta \to 0$. It was established that the entropy non-homogeneity of the pulp surface determines the variation in Gibbs energy.[16]

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The aim of the present paper was to determine thermodynamic characteristics of the system studied in the course of the process and to follow the role and the effect of the entropy factors on the chemisorption of 2 OBs on pulp.

Experimental

Bleached softwood kraft pulp with initial brightness of 85.87% ISO was used. Tinopal UP (CIBA) and Leucophor AP (Clariant) were used as OBs.[1,2] The most commonly used OBs are derivatives of 4,4'-diaministilbene-2,2'disulfonic acid. The S-triazine derivatives are of particular interest as their substitutes R_1, R_2, R_3, and R_4 allow wide chemical variations. The ratio of the absolutely dry pulp to the solution was 1:50. The bleached pulp was disintegrated and then the brightening agent was added. The initial concentration of the latter, c_o, was 0.018, 0.030, 0.060, and 0.090 gOB·gpulp^{-1}. The experiments were performed at pH 8 and constant temperature of 281, 291, and 303 K. The adsorption equilibrium was established at the 5th minute of the process and was followed for an additional 20 min. Subsequent casting of the pulp suspension was carried out varying the time of withdrawal. The brightness of the samples produced was determined spectrophotometrically in accordance with SCAN-C 11:75 standard using DATA Color 2000.[3,5,16]

Results and Discussion

Theory

The adsorbent's surface may be energetically homogeneous or heterogeneous depending on its energetic state. The heterogeneous surface is uniformly or exponentially non-homogeneous. According to the model of the uniformly non-homogeneous surface, the active centres on the adsorbent's surface are distributed linearly referring to their enthalpy of adsorption.[3]

It is well recognised that the isosteric heat of adsorption, ΔH_θ, varies with the increase in the degree of surface coverage, θ, when the adsorption is proceeding on a uniformly non-homogeneous surface.

$$(-\Delta H_\theta) = (-\Delta H_o) - C\theta \tag{1}$$

where ΔH_0 is the heat evolved within the adsorption bond formation at $\theta \to 0$, while C is a constant, characterising the interval of energetic heterogeneity.[7,8,16]

For this type of surface the equilibrium constant, K_θ, depends on θ in accordance with

$$K_\theta = K_0 e^{-f\theta} \tag{2}$$

where K_0 is the equilibrium constant of adsorption at $\theta \to 0$ and f is the heterogeneity coefficient connected with the energy and entropy non-homogeneity of the surface defined by

$$f = \frac{C}{RT} + f_s \tag{3}$$

where C is a constant, characterising the interval of energy heterogeneity and f_s expresses the entropy non-homogeneity of the surface.[5,16]

It is usually assumed that the system's entropy, ΔS_θ, does not change with θ increase. This presumption does not provoke any doubts if the variation in the adsorbed compound entropy, ΔS_a, is the only effect taken into account ($\Delta S_a < 0$) as the adsorbed molecules are fixed to the adsorbent's surface and hence have few degrees of freedom. However, in the case of a chemisorption process accompanied by breaking of bonds differing in strength as well as by variation in the surface structure, the change in the adsorbent's entropy, ΔS_s, is positive and it contributes greatly to ΔS_θ.[5-9]

$$\Delta S_\theta = \Delta S_a + \Delta S_s \tag{4}$$

The adsorption will proceed with a positive or a negative change in the system's entropy depending on the predominating effect of ΔS_a or ΔS_s.[17-20]

In the case of adsorption proceeding on a uniformly non-homogeneous surface, ΔS_θ, like ΔH_θ, varies with the increase in θ. This relation is linear and is described by

$$\Delta S_\theta = \Delta S_0 \pm m\theta \tag{5}$$

where m is a coefficient characterising the interval of entropy non-homogeneity entropy and ΔS_0 is the change in entropy at $\theta \rightarrow 0$.[7,8]

$$m = \frac{\Delta(\Delta S)}{\theta} \tag{6}$$

The relationship presented by Eq. (5) should be considered as characterising the entropy non-homogeneity of the surface.

The entropy factor in the adsorption processes can be also introduced by the temperature dependence of the equilibrium constants K_θ and K_0:

$$\ln K_\theta = -\frac{\Delta H_\theta}{RT} + \frac{\Delta S_\theta}{R} \tag{7}$$

$$\ln K_0 = -\frac{\Delta H_0}{RT} + \frac{\Delta S_0}{R} \tag{8}$$

If K_θ and K_0 in the logarithmic form of Eq. (2) are substituted by Eqs. (7) and (8) the non-homogeneity coefficient f can be expressed by

$$f = \frac{(-\Delta H_0) - (-\Delta H_\theta)}{RT\theta} + \frac{\Delta S_0 - \Delta S_\theta}{R\theta} \tag{9}$$

where (ΔH_0) and (ΔS_0) are the isosteric heat of adsorption and the entropy change at $\theta \rightarrow 0$, while $(-\Delta H_\theta)$ and (ΔS_θ) refer to the functions just mentioned but at a fixed value of θ. The entropy change should differ at different sites of the non-homogeneous surface.

Taking into account Eq. (6), the expression for f (3) becomes

$$f = \frac{C}{RT} \pm \frac{m}{R} \tag{10}$$

which leads to the elucidation of the physical meaning of f_s, i.e.

$$f_s = \frac{m}{R} \tag{11}$$

Eq. (10) shows that f is determined by the energy as well as by the entropy non-homogeneity of the adsorbent's surface. The sign (-) in Eq. (10) refers to cases where the disclosure of new adsorption centres is faster than their occupation, while the sign (+) is valid when the active centres decrease in number because of the proceeding adsorption.[5−9]

Two limiting cases can be outlined:

- $C/(RT) >> m/R$, i.e. energy factors dominate the surface non-homogeneity;

- $C/(RT) << m/R-$ in this case the entropy factors have a major effect on the surface non-homogeneity. This means that the isosteric heat of adsorption may be constant, i.e. it will not depend on the adsorption centre and the degree of coverage.

Discussion

The degree of bleaching is traditionally measured in brightness points (ISO). A dimensionless quantity α has been used as an adsorbed amount defined as a relative increase in pulp sample brightness W,

$$\alpha = \frac{W - W_0}{W_0} \tag{12}$$

where W is the running brightness corresponding to a definite reaction time, and W_0 is the initial brightness in % (ISO).

The results presented are selected at one and the same values of the adsorbed amount α for both brighteners (Tinopal UP and Leucophor AP) in order to compare their characteristics.

The effect of temperature variations and time on α is followed for both brighteners. It is found that adsorption equilibrium is attained in the system and the relative increase in pulp's brightness does not vary with time. Moreover, α increases with the temperature increase.[3,5,16]

The adsorption process is studied in the range of intermediate degrees of surface coverage where the logarithmic isotherm of Temkin is valid. There the strongest binding sites, i.e. those if greatest adsorbability, tend to be filled first while those of lowest adsorbability stay practically free.[17−20] In this case the adsorption equilibrium constant K can be expressed by

$$K = \frac{1}{c_e} \tag{13}$$

where c_e is the equilibrium concentration of the OB in the liquid phase.

Table 1. Values of the adsorption equilibrium constant K as a function of the temperature and the adsorbed amount α.

	T/K					
	281	291	303	281	291	303
α	$K/(\mathrm{gOB} \cdot \mathrm{gpulp}^{-1})$					
	Tinopal UP			Leucophor AP		
0.10	36.6	54.6	66.7	40.4	49.4	60.3
0.12	22.2	29.9	36.6	29.9	36.6	40.4
0.14	12.2	16.4	22.2	22.2	27.1	29.9
0.16	6.6	9.9	12.2	16.4	20.1	22.2

The values of K are estimated (Eq. (13)) at different adsorbed amounts of the OB expressed through the dimensionless quantity α. They are summarised in Table 1. It is seen that K increases with the temperature increase, which verifies the observed endothermic chemisorption. The values of K decrease with the increase in the adsorbed amount α (Eq. (2)).

The temperature dependence of K (Figure 1) at $\alpha = \mathrm{const}$ provides the calculation of the isosteric heat, ΔH, and the entropy, ΔS, at a fixed degree of adsorption. Linear plots $\ln K$ vs. $1/T$ are also obtained for the rest of the α values studied.
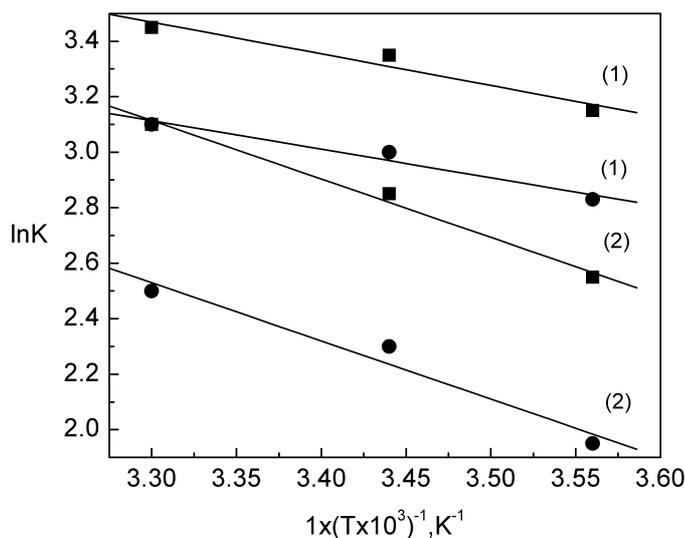
Figure 1. Temperature dependence of the equilibrium constant at ($\blacksquare$) $\alpha = 0.14$ and ($\bullet$) $\alpha = 0.16$, where (1) denotes the lines for Leucophor AP and (2) the lines for Tinopal UP.

It is found that ΔH is 15.0 kJ·mol^{-1} in the case of Leucophor AP adsorption, while it is 17.5 kJ·mol^{-1} when the Tinopal UP effect is investigated. It should be underlined that the values of ΔH do not depend on α and in fact coincide with those determined from the temperature dependence of the equilibrium constant K_0 at $\alpha \to 0$, i.e. $\Delta H_0 = \Delta H$. Hence it can be concluded that from the energetic point of view the pulp surface behaves as a uniform one. It is worth adding that the adsorption heat is generally an additive term, i.e. ΔH

$= (\Delta H_{disclosure}) + (-\Delta H_{occupation})$. It is determined by the heat evolved at adsorption centres occupation $(\Delta H_{occupation})$ as well as by the heat required for surface bonds rupture and disclosure of new adsorption centres $(\Delta H_{disclosure})$. If $|\Delta H_{occupation}| < |\Delta H_{disclosure}|$ the overall change in adsorption heat is positive and the observed process is endothermic.

In view of the aim of the present study it is of interest to determine the change in adsorption entropy ΔS at various values of α (Eq. (5)).
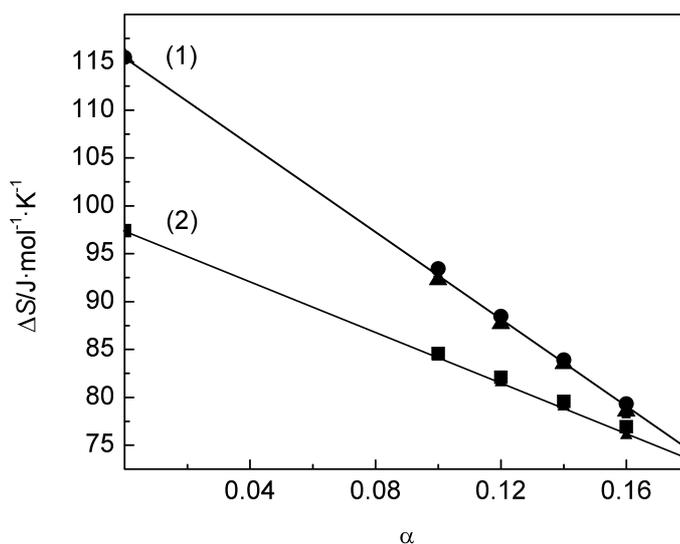
Figure 2. Plots ΔS vs. α at the temperature values studied where line (1) is for Tinopal UP and line (2) is for Leucophor AP. The symbols denote: ($\blacksquare$)T = 281 K; ($\bullet$)T = 291 K; ($\blacktriangle$)T = 303 K.

These dependencies are presented in Figure 2 for all temperature values investigated. It is seen that the entropy values decrease with α increase and hence Eq. (5) becomes

$$\Delta S = \Delta S_o - m\alpha \qquad (14)$$

The values obtained for the entropy ΔS_0 at $\alpha \to 0$ are 97.4 J·mol^{-1}·K^{-1} and 115.5 J·mol^{-1}·K^{-1} for Leucophor AP and Tinopal UP, respectively.[16]

The adsorption proceeds through rupture of hydrogen type bonds between the hydroxyl groups of adjacent chains in the pulp, which results in the disclosure of new OH-groups, i.e. new adsorption centres. The latter are accessible to the molecules of the brighteners because of their small dimensions and high mobility.[10−15] The bonds discussed are formed between the hydrogen of the hydroxyl groups of the pulp and the oxygen or the nitrogen of the polar groups of the brighteners, which is verified by the ΔH-values obtained. Hence the adsorption takes place through disclosure and occupation of the adsorption centres on the pulp surface. In the course of the process this possibility starts to decline because of the sites occupation and the steric hindrance that developed. This explains the decrease in ΔS with α increase (see Eq. (14)). The positive sign of ΔS-values can be explained by the increased degrees of freedom of the OB's molecules in their adsorption state. In fact these degrees of freedom provide the fluorescent action of the OB.

The values of coefficient m that characterised the interval of entropy non-homogeneity are estimated as well. They are 127.3 J·mol^{-1}·K^{-1} and 233.3 J·mol^{-1}·K^{-1} for Leucophor AP and Tinopal UP, respectively.

The dependence of $\Delta(\Delta S)$ on α following Eq. (6) is shown in Figure 3 at 291 K. Similar plots are obtained for the rest of the temperature values studied.
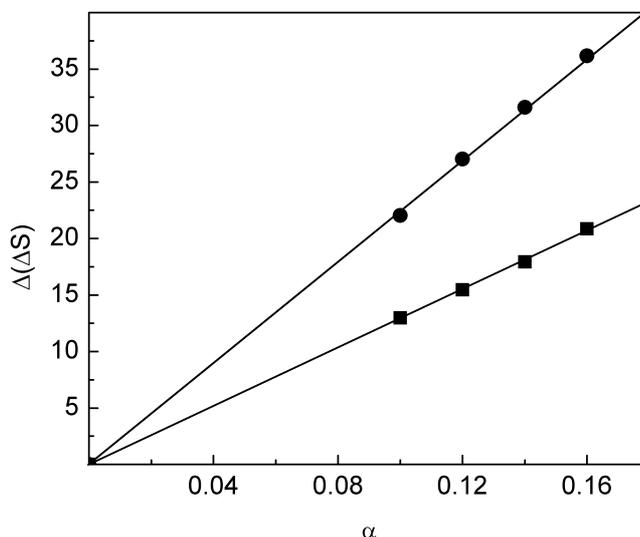
Figure 3. Plots $\Delta(\Delta S)$ vs. α at T = 291 K. The symbols denote: ($\bullet$) Tinopal UP ($\blacksquare$) Leucophor AP.

The adsorption in the OB-pulp systems takes place in the direction of the Gibbs free energy (ΔG) decrease because it is in fact a spontaneous process. The values of ΔG are calculated following the well-known equation $\Delta G = \Delta H - T\Delta S$.

The results obtained at fixed values of α and temperatures are presented in Table 2. It is seen that the entropy non-homogeneity of the pulp surface determines the variation ΔG irrespective of the positive values of ΔH.

Table 2. Variation of the Gibbs free energy ΔG as a function of the temperature T and the adsorbed amount α.

	T/K					
	281	291	303	281	291	303
α	$\Delta G/(\text{kJ.mol}^{-1})$					
	Tinopal UP			Leucophor AP		
0.10	-8.4	-9.7	-10.5	-8.8	-9.6	-10.3
0.12	-7.2	-8.2	-9.1	-8.1	-8.8	-9.4
0.14	-6.0	-7.0	-7.8	-7.4	-8.1	-8.7
0.16	-4.5	-5.6	-6.3	-6.6	-7.3	-7.8

It is also seen that the affinity of Leucophor AP towards the pulp's surface is greater than that of Tinopal UP. It can, in general, be concluded that the entropy non-homogeneity developed on Leucophor AP introduction is less while the affinity obtained is greater and hence this brightener can be considered superior when compared to Tinopal UP.

Conclusion

The values of adsorption equilibrium constant are estimated at different adsorbed amounts for 2 OBs. It is found that the overall change in adsorption heat is positive, does no depend on α, and the observed process is endothermic. The entropy values decrease with α increase because of the sites occupation and the steric hindrance that developed. The entropy non-homogeneity of the pulp surface plays the major role for determination of the Gibbs free energy.

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