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METHANOL SORPTION ON FREEZE-DRIED STARCH GEL

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Sorption isotherms and swelling curves of methanol and water on freeze-dried starch gel were determined. The obtainded results for methanol were analysed using theory relating to sorption of gases on polymers with the coupling between sorptional and conformational degrees of freedom.

INTRODUCTION

The problem of association of polar molecules as water and alcohols with amorphous regions of starch is still insufficiently recognized. Especially, it would be desirable to know the mechanism of interaction between polar molecules and separated parts of polymer chains of macromolecular components of starch [11, 13].

The process of adsorption as a bulk adsorption on polymers for water and alcohols can be described on the basis of the theory of Flory and Huggins [1]. This theory also applies to effects of swelling in amorphous regions. Rogers et al [6, 9] modified Florcy's theory of heterogenous systems. Others authors used several modified theories as BET (Brunauer-Emmett-Teller) [8, 13], GAB (Guggenheim-Anderson-De Boer) [10] in order to describe the sorption process of polar molecules on starch. In spite of a good formal coincidance of the above theories with experimental data, the disadvantage of some of them is the assumption that sorbent is inert during the sorption process. This assumtion is not true in the case of polymeric sorbents, being an obstacle for understanding the mechanism of interaction between sorbate molecules and the polymer.

From the theory [5] relating to the coupling between sorptional and conformational degrees of freedom in sorbate-sorbent chains systems, it appears that the above coupling can result in changes of shape of the sorption isotherm from type I to type III according to classification by Brunauer. Moreover, direct observations of collaps effects in sorption process on freeze-dried starch gel [12] and the changes of conformational states of biomolecules recorded by infrared spectroscopy [3] confirmed the coupling sorption-conformation effects.

The aim of this paper is to study sorption of water and methanol on freeze-dried starch gel and to apply the more realistical description of sorption related to the internal structure of the sorbing polymer.

MATERIALS AND METHODS

The study was carried out with freeze-dried starch wheat gel. The samples were prepared by dissolving the starch in water (concentration 5% and density 0.065 g/cm³). The solution was kept boiling 1 hour and stirred simultaneously to get homogenity of the solution. Then samples were aged for 100 hours in desiccator with saturated water vapour at 23°C. Then samples were cooled to -50°C, dried under vacuum in lyophilizator set during 72 hours. Finally, they were dried in the oven at 100°C for 24 hours for relaxation. The samples were formed into rods of 6 mm diameter and 11 cm length.

Water and methanol were used as sorbats. The sorption isotherms and swelling curves were performed using the method of gravimetry [4]. The vacumm equipment contained quartz spring of ca 70 mm/g sensitivity. Changes of weight and length of the samples were measured using catetometer KM-8. Amoount of sorbate in the examined sorbent was determined as:

δ_u (amount of moles of sorbat/amount of moles monomer units dry sorbent).

RESULTS AND CONCLUSIONS

Fig. 1. displays water vapour and methanol vapour sorption isotherms on lyophilized starch gel at 25°C.

The isotherms correspond to the typical sigmoid shape for polar molecules on polysaccharides [10, 2]. It can be observed that the number of sorbate molecules bond to each glucose unit is ca three ($\delta_u \approx 3$) for water and ca one ($\delta_u \approx 1$) for methanol on the same starch gel.

Fig. 2. shows the curves of swelling freeze-dried starch gel for water and methanol vapour at 25°C. It appears that a monotonic increase in the amount of methanol in the examined starch gel leads to a monotonic increase of the size of the sorbent. However, maximum and minimum peaks could be observed on the curve of swelling when the amount of sorbate water in the same starch gel increased monotonically.

The above experimental data demonstrate that during the sorption process both methanol and water cause changes in the conformation of the polymeric chain, which forms the spatial structure of the starch gel. In order to analyse the mechanism of sorptional-conformational coupling of polar molecules in starch gel we confine our considerations to the case of sorption on methanol on lyophilizational starch gel. At this stage of studies, we do not want to discuss the case of water because, although we observe phase transition resulting from the
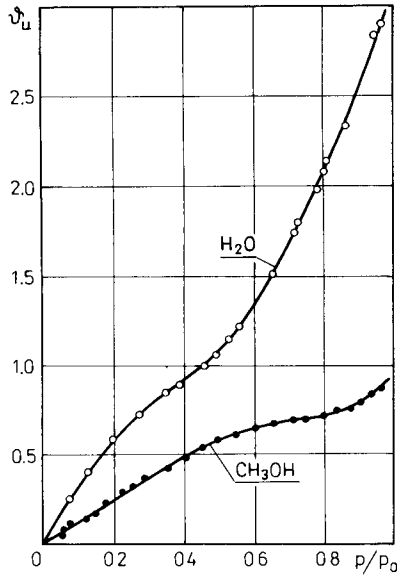
Fig. 1. Sortion isotherms of freeze-dried starch gel at 23°C for methanol (CH_3OH) and water (H_2O) vapours

coupling of sorptional-conformational subsystems. The existing sorption theories on polymers [8] can not explain the behaviour of the system when water is the sorbate.
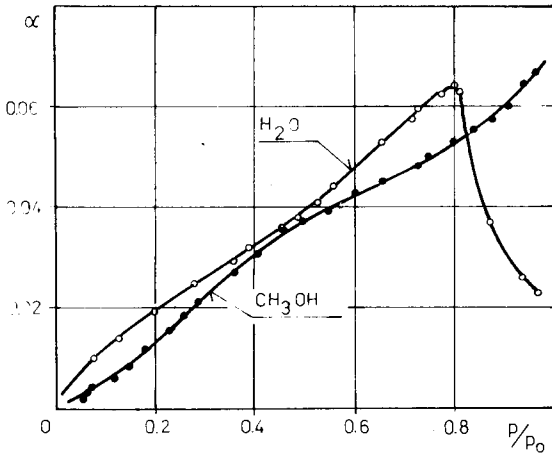

Fig. 2. Swelling ratio α versus activity of methanol and water p/p_0 at 25°C for freeze-dried starch gel

The theory of sorption of gase on polymers [5] describing monomolecular sorption on a linear chain of a polymer has been selected. This theory explains the

influence of conformational changes of a polymer on sorptional capability of sorbate, assuming that other degrees of freedom are fixed.

Let us consider sorbate-sorbent system consisting of molecules of methanol and linear chain of starch amylose. As it is generally known a polymer of amylose consists of α-D-glucose monomeric units, which are bounded to one an other by α-1,4-glycosidic linkage. Conformational changes of the whole chain of polymer can be the result of rotation round the C-O bond on the α-1,4-glycosidic linkage determined by two angles ø and ψ [7].

Conformation of each linkage between monomers can be found in one of two conformational states of energy: ground or excited [4]. There is little probability of self-transformation between conformational states because of high energy barrier. It can only happen under the influence of a sorbate molecules, i.e. by reducing the energy barrier (ca 5 Kcal/mol).

The conformations of α-D-glucose can be stabilized by hydrogen bonds inside the chain of polymer e.g. 0.3 ... 02 [7]. From experimental data, it can be assumed that one methanol molecule associates with one glucose unit and probably sorbes with OH group on CF_2OH. Consequently, the sorbed molecules interact indirectly through the conformational subsystem of the chain of amylose. For such methanol-starch system, in which we assume existence of the cooperative effect in the linear chain of polymer nad the coupling of sorptional-conformational subsystem, to describe the sorption process we can apply the equation of sorption isotherm from ref. [5] as follows:

$$
= \frac{kp/p_0}{1+kp/p_0}\left(1+\alpha_c\frac{c-1}{1+ckp/p_0}\right) \qquad \cdot \qquad (1)
$$

where:

$p/p_0 = \exp-(E-\mu)/RT, \quad k = \exp-(E-k)/RT, \quad c = \exp-c/RT, \quad$ and:
— extent of sorption ($= w\delta_u$): p/p_0 — activity of sorption; E — energy of sorption; k — energy of condensation; c — energy of coupling sorption-conformation; μ — chemical potential of the sorbate; R — constant of gases; T — temperature; α_c — function of conformation.

The values of parameters as the result of fitting the experimental data of the sorption isotherm to equation (1) are as follows: (c = −4.50; k = −0.28; A = −0.93; B = 4.58 in Kcal/mol respectivelly).
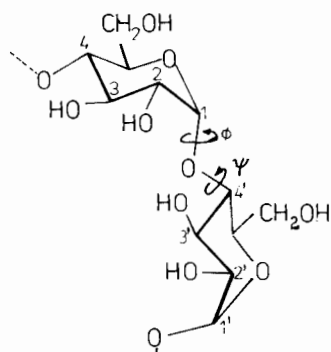
Fig. 3. Outline of geometry of α-1,4-glycosidic linkage between two α-D-glucoze residues

The agreement of experimental data with theoretical equation (1) was found ($r = 7\%$) in the range of activity $p/p_0 \varepsilon (0-0.85)$. The obtained value of the parameter C corresponds quite well to the amount of energy needed to create a new centrum of sortion on polymer. This may be connected with breaking of the hydrogen bond inside the chain of polymer e.g. 0.3 ...02 (Fig. 3.) which, in turn leads to the growth of the spatial size of the chain and to the swelling effect.
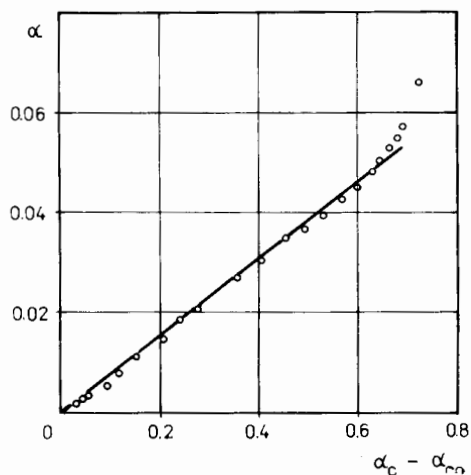

Fig. 4. Plot of swelling ratio α versus α_c-α_c° for methanol on freeze-dried starch gel

Changes of chain conformational states can be described by the monotonic function $\alpha_c = f(p/p_0, c, a, b)$ from equation (1) as:

$$\alpha_c = \frac{1}{2} + \frac{1}{2} \frac{p/p_0(abc-1)+ab-1}{[1+ab+p/p_o(1+abc)]^2-4(ab-b)(1+p/p_o)(1+cp/p_o)^{1/2}} \quad (2)$$

where: $a = \exp{-A/RT}$, $b = \exp{-B/RT}$, and: A describes the cooperative effect of chain, B corresponds to difference of energy between ground and excited states of conformation.

In the absence of any coupling sorbate-sorbent $(c = 0)$ equation (2) is reduced to the form:

$$\alpha_{\infty} = \frac{1}{2} + \frac{1}{2} \frac{(ab-1)}{[(1+ab)-4(ab-b)]^{1/2}} \quad (3)$$

and does not depend on the activity of sorbate (p/p_0).

Expression (3) describes the conformational changes of chain of sorbate molecules at a given tmeperature.

It is possible that the expression $(\alpha_c - \alpha_{\infty})$ can reflect the swelling effect in the examined system. And indeed, Fig. 4. shows a homogenous and linear dependence between the experimental swelling ratio α and the calulaled difference $(\alpha_c - \alpha_{\infty})$. It indicates that the sorption process is dominated by sorptional-conformational coupling.

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SORPCJA METANOLU NA LIOFILIZOWANYM ŻELU SKROBIOWYM

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Streszczenie

W celu doskonalenia naszej wiedzy o molekularnym mechanizmie sorpcji polarnych cząsteczek na polisacharydach przeprowadzono badania analityczne sorpcji metanolu przez liofilizowany żel skrobiowy. Otrzymane wyniki przeanalizowano stosując wcześnie opracowaną teorię, odpowiadającą sorpcji różnych rodzajów gazów przez polimery w sprzężeniu pomiędzy stopniami swobody konformacji i sorpcji. Stwierdzono, że początkowo liczba specyficznych centrów dostępnych dla sorpcji była ograniczona. Ponieważ proces sorpcji rozwija się nadal, nowe centra są aktywowane prowadząc do upłynnienia żelu, a kształt izoterm sorpcji staje się esowaty. Energetyczne parametry, według których rozwija się etap konformacyjny i sorpcyjny, określano przez dopasowanie eksperymentalnych danych izotermy sorpcji.

Okazuje się, że dla badanego systemu skrobi z częściami łańcuchów polimeru, w których wpływ kondensacji sorbenta jest ograniczony odległością pomiędzy łancuchami, system nie może być uważany jako roztwór polimeru; sprzężenie pomiędzy podsystemem sorpcyjnym i konformacyjnym odgrywa ważną rolę w procesie sorpcji, podczas której są tworzone nowe centra specyficzne.