

KINETIC PROPERTIES OF THE CHELATING DERIVATIVES OF SPHERIC CELLULOSE

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The steric effect of the functional groups on the kinetic properties of the chelating cellulose ion exchanger OSTSORB SALICYL is demonstrated. The exponential dependence was found between the diffusion coefficient and the concentration of the ion-exchanging functional groups and, together with its total mass capacity and its content of water, it has been used for the estimation of the sorbent kinetic properties. Moreover, the results obtained show that the attempt to achieve the highest possible capacity of the ion exchanger can lead to a substantial decrease of the sorption rate.

In connection with the use of the chelating ion exchangers their kinetic properties are often subject to studies as they are very important for the application of these sorbents in praxis.

The problem whether the inferior kinetic properties of the chelating ion exchangers in comparison with the classical ones are due to the properties of the skeleton, to the steric nature of the functional groups, or to the lower rate of the chelate formation in comparison with the ion exchange rate, has not yet been solved.

This study deals with the sorption rate as a function of the sorbent capacity and porosity of a series of samples of the chelating ion exchangers with a similar character of the skeleton formed by the spheric cellulose and with salicylic acid as the functional group.

THEORETICAL

The equation describing the exchange rate on ion exchangers were derived and published in the paper¹ and worked out in detail by other authors²⁻⁴. In these papers the relations for the time dependence of the exchange degree controlled by various processes (by the diffusion of the ion through the layer surrounding the sorbent particle, by its diffusion through the particle, and by the chemical reaction between the sorbed ion and the ion previously bound to the functional group) are presented together with the conditions under which the diffusion of the ion through the sorbent particle becomes the rate-determining process of the exchange kinetics (*i.e.*, the concentrations of the sorbed ion in the solution, its flow rate, the size of the sorbent grains, *etc.*).

In the case of the ion exchange rate determined by the diffusion through the particle, the exchange degree of the ion exchanger as a function of time is given by the equation¹

$$F = 1 - (6/\pi^2) \sum_{n=1}^{\infty} (1/n^2) \exp(-Dn^2 \pi^2 t/r^2). \quad (1)$$

Using an approximation of this equation a relation can be obtained from which it follows that the exchange degree F is a linear function of the square root of time (assuming that the exchange rate is determined by the diffusion through the particle).

In the paper⁵ the following equation was presented,

$$Bt = 2 - \pi^2 F/3 - 2\pi(1 - F/3)^{1/2}, \quad (2)$$

where

$$B = D \pi^2 / r^2. \quad (3)$$

Eq. (2) gives the parameter B as a function of the exchange degree F and of the time t for the values of the exchange degree ranging from 0 to 0.85.

If the diffusion through the particle is the rate-determining process, the parameter B is a constant for all pairs of F and t . Eq. (3) can be then used for the computation of the diffusion coefficient from the value of this parameter.

The exchange half-life $t_{0.5}$ that can be determined from the dependence of the exchange degree on time or on the square root of time can be used as another suitable criterion for the evaluation of the kinetic properties of the ion exchanger.

The measurement of the sorbent ion exchange rate under the conditions of the diffusion through the particle as the rate-determining process brings forth many advantages as the kinetic data obtained characterize the effect of the ion exchanger structure on its kinetic properties.

The sorbent diffusion coefficient (and therefore also the exchange half-life) depends on various parameters (*e.g.*, on the sorbed ion properties, on the solution properties, on the selectivity of the ion exchanger, on its porosity, *etc.*)⁴. Many of them play an important role, particularly in the case of chelating ion exchangers.

The Effect of the Ion Exchanger Functional Groups Concentration on its Diffusion Coefficient

The functional groups of the chelating ion exchangers are more voluminous than the functional groups of classical ion exchangers. Also the chelate formed has larger dimensions. This fact could have an effect on the kinetic properties of some chelating ion exchangers. Large molecules of functional groups and of the formed chelates can hinder the diffusion of ions into the center of the ion exchanger particle. Moreover, the presence of a high number of chelating groups has a substantial effect on the sorbent swelling and therefore also on the volume and dimensions of pores.

Let us define the quantity

$$a = (Q_A/W.R.) \rho_{H_2O} \quad (4)$$

that expresses the mass amount of the functional groups in the volume unit of pores in the ion exchanger. The existence of a relation between the value of this quantity a and the sorbent diffusion coefficient is highly probable.

The presumed relation should fulfil the following conditions:

$$1. \lim_{a \rightarrow \infty} D_{(a)} = 0 \quad (5)$$

$$2. \lim_{a \rightarrow 0} D_{(a)} = D_0 = \max [D_{(a)}]. \quad (6)$$

These conditions are met by the exponential dependence of the type

$$D = D_0 \exp(-ka). \quad (7)$$

In the logarithmic form we obtain a linear dependence

$$\ln D = \ln D_0 - ka. \quad (8)$$

Verification of this dependence was the aim of this study.

The Effect of the Ion Exchanger Capacity on its Swelling

Due to their voluminous molecules the functional groups of chelating ion exchangers occupy a substantial part of the porous sorbent. Hence, they can cause a decrease of the swelling ability of the ion exchanger and deteriorate its kinetic properties. This effect could probably take place in the ion exchangers with a hydrophilic skeleton, particularly in the case when a hydrophobic group (*e.g.*, an aromatic nucleus) is introduced into the skeleton together with the functional group.

The effect of the increasing capacity of the ion exchangers with an identical skeleton (the experiments were made with samples taken in various time intervals from the same preparation operation so that they differed only by the conversion degree of the bound functional groups) on the water content in the swelled ion exchanger was studied and the dependence obtained could be expressed by a polynomial of the second degree, *i.e.*, in the following form:

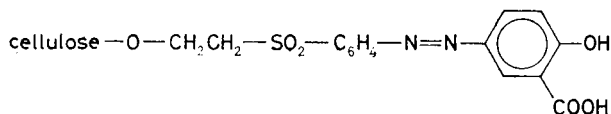
$$W.R. = A_1 Q_A^2 + A_2 Q_A + A_3. \quad (9)$$

EXPERIMENTAL

Sorbent Description

All measurements were made using the ion exchanger Ostsorb salicyl (United Chemical and Metallurgical Works, Ústí nad Labem). The basic skeleton of this sorbent is formed by the spheric cellulose^{6,7} on which an aromatic amine⁸ is bound. Its diazotation and subsequent copulation with the chelating agent is used for the preparation of a series of various chelating sorbents.

The Ostsorb salicyl structure can be schematically described by the formula



Ion exchanger of the grain size 0.315–0.40 mm in swelled state was used for the experiments. Before sieving it was washed by 15 volumes of NaOH ($c = 0.5 \text{ mol l}^{-1}$) per 1 volume of the ion

exchanger and finally by demineralized water. The use of the Na^+ form in sieving is possible as no substantial differences of the grain size between the Na^+ and H^+ forms were observed.

Determination of the Total Exchange Capacity of the Sorbent Using Cupric Ions

The Samuelson column was filled with 2 ml of the swelled ion exchanger in Na^+ form. The ion exchanger was saturated with 50 ml of CuSO_4 ($c = 0.5 \text{ mol l}^{-1}$) at the flow rate of 1–2 ml $\cdot \text{min}^{-1}$. The sorbent was washed with 50 ml of demineralized water and then the bound Cu^{2+} ions were washed out by 50 ml of HCl ($c = 2 \text{ mol l}^{-1}$). The acid was washed out by 50 ml of demineralized water. The eluate, together with the water, was caught in a volumetric flask of the volume of 250 ml. The amount of washed-out cupric ions was determined by atomic absorption spectrometry using the apparatus Varian AA-775 at $\lambda = 327.4 \text{ nm}$, with the slit width of 0.5 nm with a bent burner with an acetylene–air flame using the method of modelled calibration curve.

Measurement of the Cupric Ion Sorption Rate

The ion exchanger from the column was — after the determination of the capacity — transformed into the Na^+ form and quantitatively transferred into the filtration joint (Conannk type) with the glass frit S1, in which the kinetic measurements were made, using the method of infinite volume⁹. The joint was connected with a stopper closed with a three-way stopcock. In one position the CuSO_4 solution ($c = 0.05 \text{ mol l}^{-1}$), in the other one the demineralized water, could pass. The flow rate of both these media was adjusted so that the ion exchanger on the glass frit was continuously stirred and the concentration of the CuSO_4 solution did not practically decrease during the exchange. The time interval during which the CuSO_4 solution passed through the ion exchanger was measured by stop-watch. After the exchange the ion exchanger was immediately washed by demineralized water (by changing the position of the stopcock). The ion exchanger was then quantitatively transferred again into the column and the bound cupric ions were washed out by 50 ml of HCl ($c = 2 \text{ mol l}^{-1}$) and after washing the ion exchanger twice with 50 ml of demineralized water their content in the eluent was determined by the atomic absorption spectrometry.

The exchange degree F was calculated from Eq. (10),

$$F = c_{(t)}/c_{(\infty)} \quad (10)$$

The measured dependence F vs \sqrt{t} was linear so that the assumption of the gel diffusion as the rate-determining step of the sorption kinetics has been verified. The diffusion coefficient D was calculated from the slope B of the straight line according to the Eq. (3).

RESULTS AND DISCUSSION

The Effect of the Concentration of the Functional Groups in the Sorbent on its Kinetic Properties

The measurement of a series of ion exchanger samples on the basis of spheric cellulose with the salicylic acid as a functional group showed that the capacity and the water content of this ion exchanger have a substantial influence on the exchange rate. The correlation of the diffusion coefficient with the parameter a was obtained (the correlation coefficient = 0.950). Its shape corresponds to the shape proposed by the

theory (Fig. 1). The least square treatment of the experimental results yielded the constants of the correlation function and the hypothetic diffusion coefficient of the

TABLE I

Diffusion coefficient D as a function of the mass amount of functional groups in the volume unit of pores a

Sample No	a mmol ml^{-1}	$D \cdot 10^6$ $\text{cm}^2 \text{s}^{-1}$
1	0.07193	1.8569
2	0.08336	1.9834
3	0.12268	1.6328
4	0.15507	1.6055
5	0.16201	2.1780
6	0.16800	1.4224
7	0.16989	1.1293
8	0.16996	0.9188
9	0.18271	1.1539
10	0.19840	0.9284
11	0.20443	0.9205
12	0.22769	1.0848
13	0.23970	0.7885
14	0.24619	0.7116
15	0.30840	0.5779
16	0.32453	0.4589
17	0.34357	0.7072
18	0.43971	0.2465
19	0.45433	0.2600

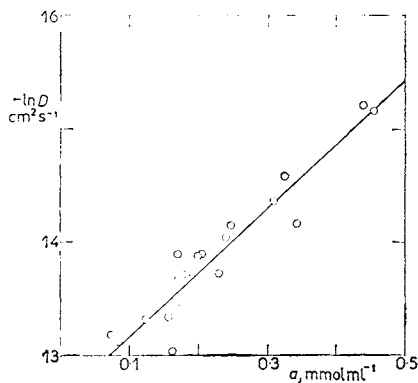


FIG. 1

Diffusion coefficient D as a function of the mass amount of functional groups in the volume unit of pores a

skeleton, $D_0 = 3.414 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. The measurement results are summarized in the Table I.

The Effect of the Sorbent Capacity on its Swelling Ability

From Table II it turns out that the content of water in the ion exchanger decreases with the increasing capacity. This fact could be probably explained by the steric effects of the chelating functional groups.

The dependence can be expressed by the Eq. (9) with the constants $A_1 = 0.9492 \text{ g}^2 \cdot \text{mmol}^{-2}$, $A_2 = -2.5306 \text{ g mmol}^{-1}$, $A_3 = 4.4862$.

It has been proved that there is a significant correlation between the concentration of functional groups in the Ostsorb salicyl ion exchanger and its diffusion coefficient. At the same time it has been proved that the swelling ability of this ion exchanger decreases with the increasing capacity.

These results mean that the increase of capacity leads to the decrease of the sorption rate. It can be assumed that a similar dependence is valid also for other sorbents with functional groups of a similar character. It seems probable that it will be necessary to choose a suitable compromise between the capacity and kinetic properties of the sorbent during its preparation. The choice of suitable parameters depends on the purpose of the ion exchanger use.

TABLE II
Dependence of the mass exchange capacity of the ion exchanger on its swelling ability

Sample No	Q_v^a	$W.R.^b$	T^c
1	0.2019	3.9925	20
2	0.2570	3.9068	40
3	0.3717	3.7015	60
4	0.4619	3.5331	80
5	0.5542	3.3725	100
6	0.5937	3.3141	120
7	0.6600	3.2753	140
8	0.6605	3.1701	160
9	0.7949	3.1632	180
10	0.7677	3.1102	200
11	0.7810	3.0700	220
12	0.7560	3.0339	240

^a Analytical mass exchange capacity, mmol Cu/g (ref.¹⁰); ^b swelling ability of the ion exchanger (minimum amount of water in g that can be contained in 1 g of the dry ion exchanger^{11,12}); ^c time interval of the ion exchanger synthesis (min).

LIST OF SYMBOLS

A_1, A_2, A_3	— correlation constants defined by Eq. (9)
a	— quantity defined by Eq. (4)
B	— parameter defined by Eq. (3)
$c_{(t)}$	— Cu^{2+} ion concentration in the ion exchanger in time t
$c_{(\infty)}$	— Cu^{2+} ion concentration in the ion exchanger in the equilibrium
D	— ion diffusion coefficient in the particle
D_0	— hypothetical diffusion coefficient calculated according to Eq. (8) for the skeleton without any functional groups
F	— exchange degree
k	— correlation constant defined by Eq. (7)
Q_A	— analytical mass exchange capacity ¹⁰
r	— particle diameter
t	— sorption time
$t_{0.5}$	— half-life of the exchange
$W.R.$	— swelling ability of the ion exchanger; maximum amount of water in g that can be contained in 1 g of dry ion exchanger ^{11,12}

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