

Adsorption of iodine on cationic cross-linked starches

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The influence of the degree of substitution (DS) on the equilibrium adsorption of iodine on cationic cross-linked starch chlorides (CCSCL) and cationic cross-linked starch iodides (CCSI) from aqueous iodine – potassium iodide solutions at different temperatures has been investigated and compared with iodine adsorption on only cross-linked starch (CS). The Langmuir, Freundlich and Dubinin–Radushkevich adsorption models have been used to describe iodine adsorption on CCSCL and CCSI. With increasing the DS, both the sorption capacity of CCSCL and CCSI and the value of effectiveness of cationic groups in iodine binding were increasing. The thermodynamic characteristics of iodine adsorption on CCSCL, CCSI and CS have been evaluated. Iodine adsorption on CCSCL and CCSI proceeded spontaneously as indicated by the calculated values of the Gibbs free energy (ΔG°). On the contrary, iodine adsorption on CS was accompanied by a positive value of ΔG° .

Key words: cationic cross-linked starch, iodine, equilibrium adsorption

List of symbols: C_{Ae} – amount of adsorbate adsorbed per one dm^3 of solution at equilibrium (mol/l), C_e – equilibrium concentration of solute in the bulk solution (mmol/l), $C_{e \text{ ads. exp.}}$ – equilibrium concentration of iodine in the bulk solution (g/l) before the evaluation of iodine hydrolysis, C_o – initial concentration of the solute in the bulk solution (mmol/l), CCS – cationic cross-linked starch, CCSCL – cationic cross-linked starch chloride, CCSI – cationic cross-linked starch iodide, CS – cross-linked starch, DS – degree of substitution, calculated according to N-(2-hydroxypropyl)-3-N,N,N-trimethylammonium groups, EF – effectiveness of cationic groups in iodine binding (mol I_2 /mol), EPTMAC – 2,3-epoxypropyltrimethylammonium chloride, E_{DR} – Dubinin–Radushkevich mean free energy of adsorption (kJ/mol), ΔG° – Gibbs free energy of adsorption (kJ/mol), ΔH° – change of enthalpy (kJ/mol), K_C – thermodynamic distribution constant, K_F – Freundlich constant concerned with the relative adsorption capacity, K_L – Langmuir equilibrium constant (l/mol), n_F – Freundlich constant concerned with the intensity of adsorption, q_e – amount of the adsorbate adsorbed by adsorbent at the equilibrium (mmol/g), Q_{DR} – Dubinin–Radushkevich saturation capacity (mmol/g), Q_L – Langmuir maximum adsorption capacity (mmol/g), R – universal gas constant (J/mol · K), R^2 – linear correlation coefficient, R_L – Langmuir dimensionless constant (the separation factor), ΔS° – change of entropy (kJ/K · mol), T – temperature (K). *Greek symbols:* β – constant related to the Dubinin–Radushkevich mean free energy (mol²/kJ²), ϵ – Polanyi potential (J/mol).

1. INTRODUCTION

The iodine–starch interaction and the formation of blue starch–iodine or amylose–iodine complexes have been studied extensively and are widely used for the determination of amylose content in starches. The starch–iodine complex con-

sists of a linear array of iodine atoms occupying the cavity of a helical amylose molecule [1]. In this form, amylose is referred to as V-amylose and has single, left-handed helices with an internal cavity where the complexed ligand can reside [2]. The iodine crystals are sparingly soluble in pure water; therefore, the conventional method of amylose–iodine complex preparation involves the addition of potassium iodide (KI) to increase the solubility of iodine in water. Although Calabrese

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and Khan [3] obtained the amylose–iodine complex in aqueous solution without adding KI, in most of the papers it has been emphasized that iodide ions are essential in initiating complexation between amylose and iodine and they are involved in the formation of amylose–iodine complexes [4–7]. An amylose–iodine complex can be prepared also under anhydrous conditions during the interaction of amylose with iodine vapour [8]. The presence of iodide in such a formation of a complex was detected by Rendleman [6] who suggested that the source of iodide was molecular iodine hydrolysis by water hydration in the starch. A similar presumption has been done in investigating gaseous iodine adsorption by solid polydiallyldimethylammonium (PDADMA) salts [9]. The equilibrium of the amylose–iodine complex formation is highly complicated, depending upon both amylose and iodine chain length. Using the classical method of potentiometric titration, it has been determined that pure amylose can accommodate 19–20% of its weight with iodine [10]. However, according to the reverse potentiometric titration, i. e. addition of amylose to a system containing an excess of iodine, this amount was increased by half, i. e. to about 30% of the amylose weight [11]. Murdoch [6] has found that anhydrous V-amylose can absorb as much of iodine vapour as about 30% of its own weight. Meanwhile, the iodine-binding capacity of amylose, determined by Calabrese and Khan, was 26% [3]. Also, iodine can form blue complexes with other natural or synthetic polymers such as glycogen [12], α -cyclodextrin [13] and poly(vinyl) alcohol [14, 15].

Another kind of polymer–iodine complexes is charge-transfer complexes. Polyvinylpyrrolidone has been known since long to interact with iodine producing a stable complex (povidone–iodine) which has been largely employed as an antiseptic [16]. Polyurethane–iodine [17], iodine–nylon-6 [18] and iodine–poly(2-vinylpyridine-co-styrene-co-divinylbenzene) [19] charge-transfer complexes were also reported in literature, and their antibacterial properties are pointed out.

In stable iodine solutions, i. e. in the presence of iodide ions and at $\text{pH} < 7$, the formation of triiodide (I_3^-) and/or pentaiodide (I_5^-) can take place. However, Gottardi [20] emphasized that, for iodophoric preparation, only interactions of polymer molecules with I_2 , I_3^- and I^- are important. Anion exchangers with strong basic properties adsorbed polyiodides (containing up to 4.75 molecules of iodine) directly from water solutions, and the rate of interaction between such substances was high [21]. Moreover, anion exchanger with iodide as a counter-ion adsorbed iodine more effectively as compared with that of the chloride counter-ion [21, 22]. In aqueous solution, in the presence of KI, quaternary ammonium groups of PDADMA salts rapidly attached iodine during the formation of polymer–iodine PDADMAI $^+$ -complexes I_m^- ($m \leq 4$) and PDADMA iodide adsorbed iodine more effectively than did PDADMA chloride or bromide [9]. Insoluble iodine-saturated materials with primary, secondary, tertiary amino or quaternary ammonium groups are suggested as bactericides for water treatment [23, 24].

Starch is a low-cost natural renewable polymer that can be cross-linked with epichlorohydrin and cationised with 2,3-epoxypropyltrimethylammonium chloride with a high reaction efficiency [25]. It was established that the obtained cationic cross-linked starches (CCS) with the degree of substitution (DS) from about 0.2 to 0.6 can adsorb from aqueous solutions anionic dyes [26], anionic complexes of disperse dyes and dispersing agents [27], and hexavalent chromium [28, 29]. The effectiveness of cationic groups in binding adsorbate (EF) depend on both the nature of the adsorbate and the properties of CCS. Depending on the DS and the degree of cross-linking of CCS and the origin of native starch used to prepare CCS, CCS with different particle size and different EF values were obtained. It could be suggested that CCS would also act as efficient adsorbents of anionic species of iodine from water solutions.

In this paper, the influence of DS of CCS and the impact of chloride and iodide counter-ions of quaternary ammonium groups of CCS on the equilibrium iodine adsorption process have been investigated alongside with the effect of adsorption temperature. The Langmuir, Freundlich and Dubinin–Radushkevich adsorption models have been used to assess the adsorption data, and also the thermodynamic characteristics have been evaluated.

2. MATERIALS AND METHODS

2.1. Materials

The native potato starch (Antanavas Starch Plant, Lithuania) was dried at 104 °C before use. 2,3-epoxypropyltrimethylammonium chloride (70%, Fluka), epichlorohydrin (99%, Aldrich) were used as received. I_2 -KI fixanal and KI fixanal were purchased from Fluka.

2.2. Preparation of CCS chlorides

The molecular mass of the anhydroglucoside unit (AGU) was assumed as a mole of starch. The starch was cross-linked with 0.1 mol/AGU of epichlorohydrin (EPCH) in the presence of sodium hydroxide, washed with cold water, dried and then cationized with 2,3-epoxypropyltrimethylammonium chloride (EPTMAC) in the presence of sodium hydroxide as a catalyst (the molar ratio AGU : EPTMAC : catalyst : H_2O was 1 : 0.2–0.6 : 0.04 : 16) at 45 °C for 24 h. After the reaction, CCS chloride (CCSCL) was washed 5 times with water and 2 times with water–isopropanol mixture and dried. The number of cationic groups in CCSCL was expressed as the degree of substitution (DS), which was calculated from the nitrogen content estimated by the Kjeldahl method [30] after purification by Soxhlet extraction with methanol for 16 h.

2.3. Preparation of CCS iodides

The dry CCSCL was poured over KI solution and mixed with a magnetic stirrer for 2 h. The molar ratio of CCSCL (according to cationic groups) and KI in the solution was 1 to 1.5. After adsorption, the suspension was filtered through glass

filter, washed with distilled water until no traces of Cl^- or I^- in the filtrate were detected, dried and the nitrogen content was estimated by the Kjeldahl method. The content of iodide in the prepared CCSI was calculated by evaluating the nitrogen content in CCSCI before and after iodide adsorption.

2.4. Equilibrium adsorption studies

Iodine–potassium iodide (I_2 -KI) and KI solutions were prepared from I_2 -KI fixanal (molar ratio of I_2 to KI was 1 to 3) or KI fixanal by dilution with distilled water to get the required concentration. The pH of I_2 -KI and KI solutions was in the range of 5.4–5.6 in all experiments.

0.1 g of dry CCSCI (or the amount of CCSI that has an equivalent number of quaternary groups as 0.1 g CCSCI) was placed into an Erlenmeyer flask, and 100 cm^3 of I_2 -KI or KI solution of desired concentration was added. The flask was stoppered and shaken for 30 min at different temperatures and at a fixed shaking intensity in a thermostated water bath with a temperature control of $\pm 1 \text{ }^\circ\text{C}$ (Mettler GmbH, Germany). Then the mixture was filtered through a glass filter, and the residual concentration of iodine or iodide in the solution was estimated. To minimize the hydrolysis of iodine (see Section 2.6), the temperature of adsorption experiments was not higher than $35 \text{ }^\circ\text{C}$.

2.5. Iodine and iodide determination

The concentration of iodine in the samples was determined by titration with sodium thiosulphate solution prepared from the fixanal. Meanwhile, the concentration of iodide in the samples was determined spectrophotometrically at 226 nm. UV absorption spectra were recorded with a Unicam UV3 UV-Vis spectrometer.

2.6. Evaluation of iodine hydrolysis

In order to evaluate the iodine hydrolysis the experiments as described in Section 2.4 have been performed at 20, 25, 30 and $35 \text{ }^\circ\text{C}$ without adding adsorbents (CCSCI or CCSI). The concentration of iodine in a solution after experiments (C_e) was determined and compared with the initial iodine concentration (C_o) (data not shown). The used temperature

was found to have a little effect on iodine hydrolysis. By linear regression analysis of C_e versus C_o , an equation with the correlation coefficient of 0.9989 was obtained. From the linear equation, the amount of hydrolysed iodine can be evaluated from the adsorption data by the following equation:

$$C_e = \frac{C_{e \text{ ads. exp.}} + 0.0222}{0.9978}, \quad (2.1)$$

where C_e is the equilibrium concentration of iodine in the bulk solution (g/l), and $C_{e \text{ ads. exp.}}$ is the equilibrium concentration of iodine in the bulk solution (g/l) before evaluation of iodine hydrolysis.

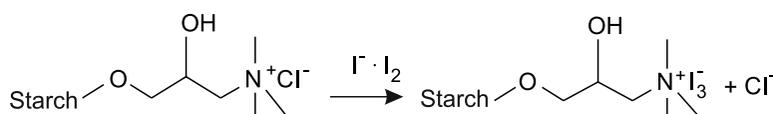
3. RESULTS AND DISCUSSION

3.1. Iodine adsorption on CCSCI and CCSI

During the reaction of cross-linked starch (CS) with EPT-MAC, cross-linked *N*-(2-hydroxypropyl)-3-*N,N,N*-trimethylammoniumstarch chloride (CCSCI) has been obtained. In stable iodine aqueous solutions, i.e. in the presence of iodide ions and at $\text{pH} < 7$, anionic species of iodine, first of all triiodide (I_3^-), could be adsorbed by quaternary ammonium groups of CCSCI according to the ion-exchange mechanism (see Scheme 1).

The same complexes of cationic cross-linked starch (CCS) and I_3^- could be obtained by a two-step adsorption process. In the first step, CCS iodide (CCSI) could be obtained by ion exchange between CCSCI and KI in aqueous solution. In the second step, the molecular iodine (I_2) could be adsorbed onto CCSI from aqueous I_2 -KI solution. It is known [9, 22] that polymers with iodide as a counter-ion of the cationic group adsorb iodine more effectively than those containing chloride or hydroxide. During ion exchange between CCSCI and KI, only 50–69% of chloride ions were replaced by iodide ions (Table 1). Despite this fact, we named CCS with mixed counter-ions as CCSI.

The influence of DS and the nature of a counter-ion alongside the temperature on the equilibrium adsorption of iodine on CCSCI and CCSI from aqueous solutions of I_2 -KI has been investigated and expressed as moles of iodine per gram of



Scheme 1. Ion exchange between CCSCI and I_3^-

Table 1. Characteristics of CCSCI and CCSI used in equilibrium iodine adsorption experiments

DS of CCS	Amount of cationic groups in the sample of adsorbent, equiv./g	Dose of CCSCI, g	Portions of chloride ions replaced by iodide ions in CCSI, %	Dose of CCSI, g
0.14	$0.715 \cdot 10^{-3}$	1.000	50	1.034
0.35	$1.614 \cdot 10^{-3}$	1.000	69	1.092
0.54	$2.215 \cdot 10^{-3}$	1.000	59	1.119

adsorbent. The molecular masses of Cl^- and I^- are different. In order to compare the adsorption results, the taken quantities of CCSCI and CCSI allowed the number of cationic groups in the sample to be the same (Table 1). The adsorption of iodine both on CCSCI and CCSI proceeds very fast, and all content of iodine was adsorbed during the first 5–10 min of the process (data not shown). In order to allow the adsorption to be completed, the experiment was extended to 30 min. During this time, the hydrolysis of iodine was not high and was evaluated according to equation (2.1) (see Section 2.6).

The adsorption isotherms of iodine on CCSCI and CCSI with DS of 0.14, 0.35 and 0.54 at different temperatures have been obtained. As an example, the adsorption isotherms of iodine on CCSCI and CCSI with DS = 0.35 are given in Fig. 1. The Langmuir, Freundlich and Dubinin–Radushkevich adsorption models have been used to describe the adsorption isotherms.

The Langmuir equation may be presented as

$$q_e = \frac{Q_L K_L C_e}{1 + K_L C_e}, \quad (\text{non-linear form}) \quad (3.1)$$

$$\frac{C_e}{q_e} = \frac{1}{Q_L K_L} + \frac{1}{Q_L} \cdot C_e, \quad (\text{linear form}) \quad (3.2)$$

where q_e (mol/g) is the amount of the adsorbate adsorbed by the adsorbent at the equilibrium, C_e (mol/l) is the equilibrium concentration of the adsorbate, Q_L (mol/g) is the Langmuir sorption capacity, and K_L (l/mol) is the Langmuir equilibrium constant. Then C_e/q_e versus C_e was plotted, and Q_L was calculated from the slope and K_L from the intercept.

The Freundlich equation may be written as follows:

$$q_e = K_F C_e^{n_F}, \quad (\text{non-linear form}) \quad (3.3)$$

$$\ln q_e = \ln K_F + \frac{1}{n_F} \ln C_e, \quad (\text{linear form}) \quad (3.4)$$

where K_F (l/mmol) is the Freundlich isotherm constant concerned with the relative adsorption capacity, and n_F is a constant related to adsorption intensity. By plotting $\ln q_e$ versus $\ln C_e$, the value of K_F was obtained from the intercept and n_F from the slope.

The Dubinin–Radushkevich isotherm equation [32] may be written as

$$q_e = Q_{DR} \exp(-\beta \varepsilon^2), \quad (\text{non-linear form}) \quad (3.5)$$

$$\ln q_e = \ln Q_{DR} - \beta \varepsilon^2, \quad (\text{linear form}) \quad (3.6)$$

where Q_{DR} (mmol/g) is the theoretical saturation capacity, β (mol^2/kJ^2) is the constant related to the mean free energy of adsorption per mole of adsorbate, and ε is the Polanyi potential equal to:

$$\varepsilon = RT \ln \left(1 + \left(\frac{1}{C_e} \right) \right). \quad (3.7)$$

Hence, by plotting $\ln q_e$ versus ε^2 it is possible to obtain the value of Q_{DR} from the intercept and the value of β from the slope. The constant β gives an idea about the Dubinin–Radushkevich mean free energy E_{DR} (kJ/mol) of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated using the relationship

$$E_{DR} = \frac{1}{\sqrt{2\beta}}. \quad (3.8)$$

The values of the most significant parameters of the adsorption models such as the Langmuir sorption capacity Q_L , the Freundlich constant n_F (related to the intensity of adsorption) and the Dubinin–Radushkevich adsorption energy E_{DR} are given in Tables 2 and 3 along with the values of the linear correlation coefficient R^2 . In order to compare the sorption properties of CCSCI, and CCSI the values of effectiveness EF

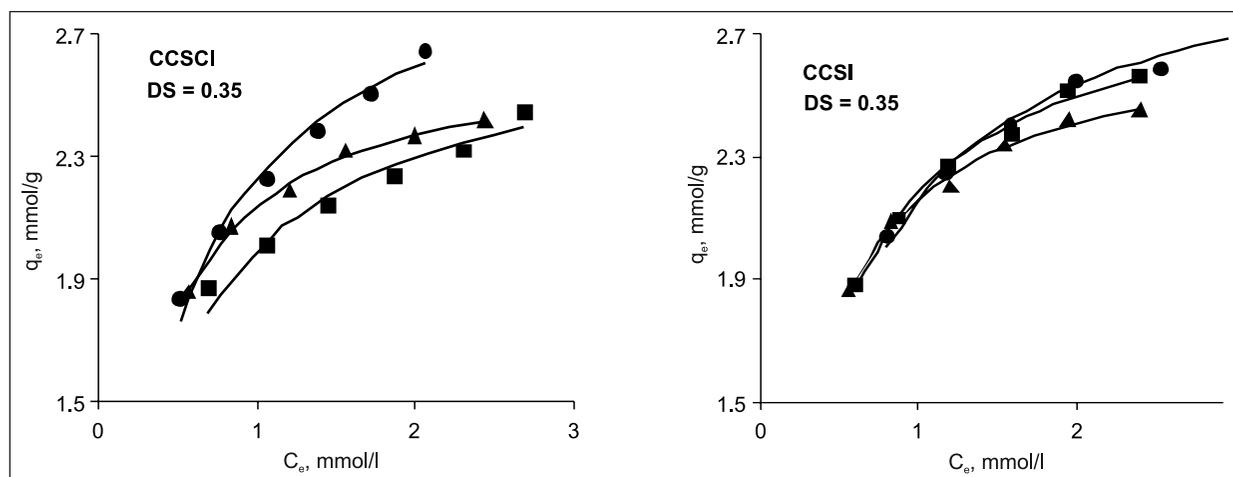


Fig. 1. Adsorption isotherms of iodine onto CCSCI and CCSI with DS = 0.35 at a temperature of 25 °C (▲), 30 °C (■) and 35 °C (●). Symbols represent experimental data and lines represent fitted curves of the Langmuir model

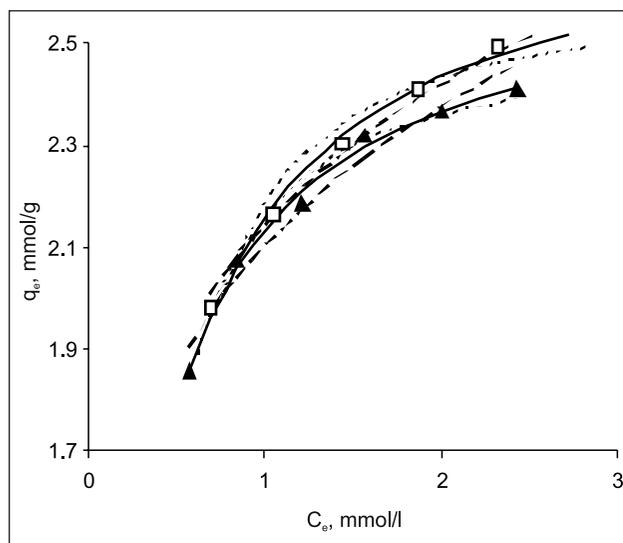


Fig. 2. Adsorption isotherms of iodine onto CCSCI (▲) and CCSI (□) with DS = 0.35 at a temperature of 25 °C. Symbols represent experimental data. Lines represent fitted curves of the models: solid line – Langmuir, dash line – Freundlich, dotted line – Dubinin–Radushkevich

of the cationic groups in the binding of iodine expressed as a mole of iodine per mole of CCS, were calculated from the Langmuir sorption capacity Q_L and are presented in Table 2. The high values of R^2 support the fact that the adsorption data closely follow the Langmuir adsorption model. Slightly lower R^2 values were obtained for the Freundlich and the Dubinin–Radushkevich adsorption models. Figure 2 presents a comparison of experimental and predicted amounts of iodine adsorbed on CCSCI and CCSI for all the isotherm models studied. It is clear that the Langmuir isotherm best fits the experimental equilibrium data.

According to the Langmuir adsorption model [31], iodine, or rather the anionic species of iodine, was adsorbed on active centres of CCSCI or CCSI, i. e. on quaternary ammonium groups. The driving forces of the adsorption were electrostatic interactions between the latter groups and the anionic species of iodine. A considerable increase in the Langmuir adsorption capacity Q_L by increasing the DS of CCSCI and CCSI (Table 2) confirms this presumption. Another important fact is that at the same DS slightly more iodine was adsorbed on CCSI than on CCSCI. As in the case of other polymers with

Table 2. Parameters of the Langmuir adsorption model for iodide adsorption on CCSCI and CCSI with different DS at different temperatures

Temperature, °C	CCSCI			CCSI		
	Q_L , mmol/g	EF , mol I ₂ /mol	R^2	Q_L , mmol/g	EF , mol I ₂ /mol	R^2
DS = 0.14						
25	1.11	1.48	0.9974	1.17	1.56	0.9994
30	1.13	1.51	0.9971	1.18	1.57	0.9988
35	1.16	1.55	0.9978	1.185	1.58	0.9993
DS = 0.35						
25	2.65	1.64	0.9997	2.88	1.78	0.9991
30	2.72	1.68	0.9967	2.96	1.84	0.9994
35	2.79	1.73	0.9979	2.98	1.845	0.9991
DS = 0.54						
25	4.22	1.91	0.9971	4.27	1.93	0.9995
30	4.35	1.96	0.9995	4.47	2.02	0.9997
35	4.54	2.05	0.9978	4.61	2.08	0.9994

Table 3. Parameters of the Freundlich and Dubinin–Radushkevich adsorption models for iodide adsorption on CCSCI and CCSI with different DS at different temperatures

Temperature, °C	CCSCI				CCCI			
	Freundlich model		Dubinin–Radushkevich model		Freundlich model		Dubinin–Radushkevich model	
	n_F	R^2	E_{DR} (kJ/mol)	R^2	n_F	R^2	E_{DR} (kJ/mol)	R^2
DS = 0.14								
25	4.2	0.9779	13.6	0.9857	5.7	0.9575	15.1	0.9636
30	4.6	0.9753	14.2	0.9854	5.5	0.9667	14.9	0.9723
35	5.4	0.9939	15.5	0.9950	4.8	0.9656	14.5	0.9694
DS = 0.35								
25	6.9	0.9655	15.3	0.9751	5.1	0.9856	14.3	0.9901
30	5.5	0.9930	14.8	0.9890	4.8	0.9880	14.0	0.9912
35	3.9	0.9993	13.2	0.9991	4.6	0.9831	14.1	0.9893
DS = 0.54								
25	7.0	0.9634	15.9	0.9534	8.3	0.9603	17.7	0.9605
30	6.1	0.9610	14.3	0.9609	7.7	0.9711	16.3	0.9598
35	6.0	0.9505	14.5	0.9582	6.5	0.9454	15.7	0.9550

strong basic groups [9, 22], iodide as a counter-ion of quaternary ammonium groups promotes iodine adsorption on CCS. Along with an increase of the total amount of adsorbed iodine, the values of EF increased, also, with an increase of DS (Table 2). One cationic group of modified starch could adsorb over one molecule of iodine, i. e. some molecules of adsorbed iodine were present in the form of I_3^- and others as I_5^- . The higher was DS, the higher portion of iodine was introduced into a complex with CCS as I_5^- . The increase in the effectiveness of cationic groups in the binding of iodine with the increase of DS could be related to changes in the hydrophobicity of modified starch microgranules during iodine adsorption. The higher DS, the higher number of cationic groups is located on the surface of microgranules and, thus, a higher number of I_3^- covers the surface with the external iodine molecules. The hydrophobicity of such microgranules increases as compared with that of CCS microgranules with lower DS. Iodine preferred the hydrophobic environment, so more hydrophobic microgranules of CCS could more easily adsorb other iodine molecules.

With an increase of the temperature, the extent of iodine adsorption both on CCSCI and CCSI increased (Table 2). The influence of temperature on the Q_L and EF values increased with an increase of DS.

Additional information about iodine adsorption on CCSCI and CCSI was obtained from the values of the Freundlich constant n_F and the Dubinin–Radushkevich adsorption energy E_{DR} . The magnitude of the exponent n_F gives an indication on the favourability of adsorption. In general, the values of n_F in the range 2–10 represent good, 1–2 moderately difficult, and less than 1 poor adsorption characteristics [33]. The Dubinin–Radushkevich adsorption energy E_{DR} gives information about the adsorption mechanism: if the value of E_{DR} is between 8 and 16 kJ/mol, the adsorption process follows the ion-exchange mechanism, and if the value of E_{DR} is less than 8 kJ/mol, the nature of the adsorption process is physical [34]. As could be seen from data in Table 3, the E_{DR} values were higher than 8 kJ/mol in all cases of adsorption and confirmed the ion-exchange mechanism between anionic species of iodine and quaternary ammonium groups of CCSCI or CCSI. With increasing the adsorption temperature, the value of E_{DR} decreased and ion-exchange became more difficult, except iodine adsorption on CCSCI with DS = 0.14. The obtained values of the Freundlich constant n_F (Table 3) are in agreement with the values of E_{DR} and confirm the favourability of iodine adsorption both on CCSCI and CCSI of various DS. Except adsorption on CCSCI with DS = 0.14, the

values of n_F decreased with increasing the temperature and supported the fact of a negative influence of temperature on the ion-exchange mechanism.

3.2. Iodine adsorption on CS

The amylose, which is present in starch, and its derivatives form blue starch–iodine inclusion complexes (Am-I) in I_2 -KI solution. For this reason, some portion of iodine adsorbed on CCS may be incorporated into the polyelectrolyte CCS-I · I_n^- complexes and another portion composes the Am-I. In order to estimate the amount of iodine introduced into Am-I, the equilibrium iodine adsorption on cross-linked starch (CS) has been investigated at different temperatures.

The adsorption isotherms of iodine on CS are presented in Fig. 3. Differently from iodine adsorption on CCS, the Langmuir adsorption model didn't fit the iodine adsorption on CS data. For this reason, in Fig. 2 lines represent the curves fitted according to the Freundlich adsorption model, and the experimental data of iodine adsorption on CS at equilibrium ($q_{e, \text{exp}}$) was given in Table 4 instead of the Langmuir sorption capacity.

The influence of temperature on the adsorbed amount of iodine was negligible. The $q_{e, \text{exp}}$ values varied from 0.20 to 0.29 mmol/g (Table 4). Suggesting from the character of adsorption isotherms (Fig. 3), it is likely that the equilibrium

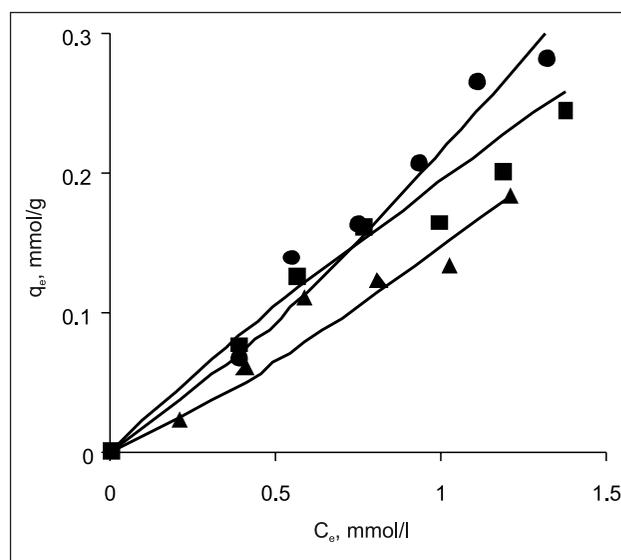


Fig. 3. Adsorption isotherms of iodine onto CS at a temperature of 25 °C (▲), 30 °C (■) and 35 °C (●). Symbols represent experimental data and lines represent fitted curves of the Freundlich model

Table 4. Amount of iodine adsorbed on CS and parameters of the Freundlich and Dubinin–Radushkevich adsorption models at different temperatures

Temperature, °C	$q_{e, \text{exp}}$, mmol/g	Freundlich model		Dubinin–Radushkevich model	
		n_F	R^2	E_{DR} , kJ/mol	R^2
25	0.20	0.85	0.9573	6.3	0.9540
30	0.29	0.91	0.9728	6.6	0.9790
35	0.24	0.83	0.9892	6.3	0.9939

of iodine adsorption on CS was not reached. However, if to take into account that the average amount of amylose in potato starch is about 20% [35] and the average value of adsorbed iodine is 0.24 mmol/g (see Table 4), the calculated value of the iodine-binding capacity (IBC) is 30.9% and coincides with the IBC value referred to in the literature [6, 11]. Therefore, all the possible amount of iodine was introduced into Am-I during adsorption experiments. A comparison of iodine amounts adsorbed on CCS and CS (see Tables 2 and 4) has shown that the part of iodine introduced into Am-I depends on the DS of CCS, and it could comprise 5 to 25% of the total amount of iodine adsorbed on CCS.

The Freundlich and Dubinin–Radushkevich adsorption models described the iodine adsorption on both CCS and CS with the same approximation ($R^2 > 0.95$, see Tables 3 and 4). However, the calculated values of the Freundlich and Dubinin–Radushkevich constants were quite different from those established for iodine adsorption onto CCSCI or CCSI. The values of adsorption energy E_{DR} were less than 8 kJ/mol and indicated that the nature of iodine adsorption on CS was physical. Moreover, the values of the Freundlich constant n_F ($n_F < 1$) confirmed that the conditions for iodine adsorption on CS were poor. These data are in agreement with the opinion that iodine into Am-I complexes is introduced by the physical, i. e. hydrophobic, forces [2].

3.3. Adsorption thermodynamics

Thermodynamic considerations are necessary to assess whether the adsorption process is spontaneous or not. Changes in the Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were determined by the following equations:

$$K_c = \frac{C_{Ae}}{C_e}, \quad (3.9)$$

$$\Delta G^\circ = -RT \ln K_c, \quad (3.10)$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}, \quad (3.11)$$

where K_c is the thermodynamic distribution coefficient, C_{Ae} is the amount of iodine adsorbed on CCSCI or CCSI per dm^3 of the solution at equilibrium (mol/l), C_e is the equilibrium concentration of iodine in solution (mol/l), and T is the solution temperature in K.

The thermodynamic distribution coefficient K_c was determined by the linear regression analysis of $\ln q_e / C_e$ versus q_e [36] (data not shown). The intersection of the straight lines with the vertical axis gives the value of $\ln K_c$, ΔH° and ΔS° were calculated from the slope and intercept of plots of $\ln K_c$ versus $1/T$. The calculated thermodynamic parameters, along with the values of correlation coefficients, are presented in Table 5 for iodine adsorption on CS and CCSCI and in Table 6 for iodine adsorption on CCSI.

The value of ΔG° gives some information about the adsorbate–adsorbent affinity and the driving forces of adsorption. The more negative is the value of ΔG° , the higher is the affinity and more spontaneously the adsorption proceeds. Moreover, according to equation (3.10), the more negative the ΔG° value, the higher is the value of the distribution coefficient, i. e. the major part of adsorbate on the adsorbent is in equilibrium. On the contrary, the positive value of ΔG° indicates that the major part of the adsorbate remains in solutions in equilibrium. This exceptional case was observed when iodine was adsorbed on CS (Table 5). The formation of a blue iodine–starch complex was accompanied by the positive value of ΔG° (from 5.8 to 4.75 kJ/mol) and a very low value of the distribution coefficient K_c in the range 0.095 to 0.156. The obtained values of ΔG° and K_c could be related to the mechanism of Am-I formation and determine the quantity of iodine introduced into Am-I.

When iodine was adsorbed on CCSCI or CCSI, the calculated values of ΔG° were negative (Tables 5 and 6), and the

Table 5. Thermodynamic parameters of iodine adsorption on CS and CCSCI with different DS

Temperature, °C	$\ln K_c$	K_c	R^2	ΔG° , kJ/mol	ΔH° , kJ/mol	ΔS° , J/mol · K	R^2
CS							
25	-2.36	0.095	0.9922	5.8			
30	-1.94	0.143	0.9599	4.9	40	116	0.9538
35	-1.86	0.156	0.9976	4.75			
CCSCI, DS = 0.14							
25	3.25	26	0.9767	-8.1			
30	3.54	34	0.976	-8.9	67	253	0.9558
35	4.14	63	0.9901	-10.6			
CCSCI, DS = 0.35							
25	5.20	181	0.962	-12.9			
30	4.56	96	0.9814	-11.5	-119	-355	0.987
35	3.64	38	0.9972	-9.3			
CCSCI, DS = 0.54							
25	5.91	367	0.9163	-15.5			
30	5.19	180	0.9526	-13.1	-168	-511	0.9999
35	4.51	91	0.927	-10.4			

Table 6. Thermodynamic parameters of iodine adsorption on CCSI with different DS

Temperature, °C	$\ln K_c$	K_c	R^2	ΔG° , kJ/mol	ΔH° , kJ/mol	ΔS° , J/mol · K	R^2
DS = 0.14							
25	4.60	100	0.9963	-11.2			
30	4.10	60	0.9393	-10.15	-76.5	-223	0.9998
35	3.08	22	0.9611	-7.9			
DS = 0.35							
25	5.74	311	0.9639	-14.0			
30	5.17	176	0.999	-12.8	-78	-228	0.9996
35	4.17	65	0.9977	-10.7			
DS = 0.54							
25	8.29	3980	0.9662	-20.2			
30	6.31	551	0.9513	-15.9	-150	-444	0.9994
35	5.27	194	0.980	-13.5			

formation of iodine complexes with cationic starches was spontaneous. The slightly more negative values of ΔG° for iodine adsorption on CCSI, especially at lower temperatures, indicate that the affinity of iodine for CCSI is slightly higher and, consequently, the higher values of K_c were observed.

The influence of temperature on changes in ΔG° depended on the DS of the adsorbent. When iodine was adsorbed on CCSCI with DS = 0.14, with increasing adsorption temperature a higher negative value of ΔG° was obtained. At the same time, iodine adsorption was endothermic, and the randomness of the system increased (positive values of ΔH° and ΔS°) as in the case of iodine adsorption on CS (Table 5). One of the reasons may be the higher quantity of iodine introduced into Am-I complexes alongside the formation of CCS-iodine complexes. When iodine was adsorbed on CCSCI with DS of 0.35 or 0.54 (Table 5) or on CCSI of various DS (Table 6), with an increase of adsorption temperature the negative value of ΔG° (i. e. the affinity of iodine to CCS) decreased. The obtained high negative values of ΔH° and ΔS° suggested the adsorption process to be exothermic, and the order of the system increased. Moreover, with an increase of DS, the negative values of ΔH° and ΔS° increased, i. e. the system underwent major changes.

4. CONCLUSIONS

The influence of DS on equilibrium adsorption of iodine on cationic cross-linked starch chlorides (CCSCI) and cationic cross-linked starch iodides (CCSI) from aqueous iodine-potassium iodide solutions has been investigated at different temperatures and compared with the data obtained for iodine adsorption on cross-linked starch (CS).

The Langmuir, Freundlich and Dubinin-Radushkevich adsorption models have been used to describe the iodine adsorption on CCSCI and CCSI. According to the Langmuir model, the anionic species of iodine was adsorbed by quaternary ammonium groups of CCSCI or CCSI. The calculated values of the Dubinin-Radushkevich adsorption energy E_{DR} and the Freundlich constant n_F confirmed the ion-exchange mechanism between anionic species of iodine and quater-

nary ammonium groups and the favourability of iodine adsorption on both CCSCI and CCSI.

With an increase of DS, the calculated values of the Langmuir sorption capacity Q_L increased both for CCSCI and CCSI. One cationic group of modified starch could adsorb over one molecule of iodine. The higher was DS, the higher amount of iodine was introduced into the complex with cationic starch as I_5^- .

The Langmuir adsorption model was not suitable to describe the adsorption of iodine on CS, i. e. the formation of a blue inclusion complex. The calculated values of E_{DR} and n_F indicated that the nature of iodine adsorption on CS was physical and the conditions for adsorption were poor.

The adsorption of iodine on CCSCI and CCSI proceeded spontaneously as indicated by negative values of the Gibbs free energy (ΔG°). On the contrary, formation of the Am-I complex was accompanied by a positive value of ΔG° .

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JODO ADSORBCIJA TINKLINIU KATIJONINIŲ KRAKMOLU

Santrauka

Ištirta pusiausvyroji jodo adsorbicija iš vandeninių jodo–kalio jodido tirpalų įvairaus pakeitimo laipsnio (PL) tinklinio katijoninio krakmolo chloridu (TKKCl) ir tinklinio katijoninio krakmolo jodidu (TKKJ) skirtingose temperatūrose, kuri palyginta su jodo adsorbicija tinkliniu krakmolu (TK). Adsorbicijai aprašyti pritaikyti Langmiuro, Freundlichio ir Dubinino–Radushkevichio adsorbicijos modeliai. TKKCl ir TKKJ sorbcinė geba ir katijoninių grupių efektyvumas sujungiant jodą didėjo didėjant jų PL. Esant tam pačiam PL daugiau jodo adsorbavo TKKJ. Apskaičiuoti termodinaminiai jodo adsorbicijos TKKCl, TKKJ ir TK rodikliai. Neigiamos Gibso laisvosios energijos pokyčio vertės (ΔG°) patvirtino, kad jodo adsorbicija TKKCl ir TKKI vyksta spontaniškai. Adsorbuojant jodą TK gautos teigiamos ΔG° vertės.