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RADIOISOTOPE STUDY OF FRUCTOSE ADSORPTION AT THE ALUMINA/ELECTROLYTE INTERFACE

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Abstract: The mechanism, kinetic and static studies of fructose adsorption at the alumina/electrolyte interface using radiolabeled ^{14}C -fructose were conducted. Pseudo 2nd order model of adsorption kinetics was found to fit best to adsorption as a function of time. The fructose adsorption was found to decrease with increasing pH of the solution. Considering the changes in concentration of surface groups at the alumina/electrolyte interface, the hydrogen bonding is the most probable mechanism of interaction of fructose with the surface. This is confirmed by calorimetric titration experiments because the measured heat of adsorption was 10.8 kJ/mol. For the system studied the coverage of surface by fructose was several times smaller than the monolayer.

Keywords: alumina, fructose, adsorption, hydrogen bonding, ^{14}C -fructose

Introduction

Saccharides and polysaccharides have been for years used as compounds that control the rheological properties of ceramic slurries or stability of dispersions (Bednarek et al., 2012; Safinajafabadi et al., 2012). They are also used as depressant in froth flotation (McFadzean et al., 2011). Besides, developments and demands of sugar based surfactants are increasing. Despite the long-time use of these compounds, the mechanism of their adsorption at the solid/electrolyte interface has not been described sufficiently. Only few papers have discussed the mechanism of saccharides' adsorption (Liu et al., 1989; Zhang et al. 2002; Singh and Mohan, 2004). Singh and Mohan consider the adsorption of monosaccharides on alumina surface according to three mechanisms: partially negative oxygen atom of a $-\text{OH}$ group of saccharide may interact with the $\equiv\text{S}-\text{OH}_2^+$ surface groups; partially negative oxygen atom of $-\text{OH}$ group of saccharide may interact with a $\equiv\text{S}-\text{OH}$ surface group via hydrogen bonding

and positively charged hydrogen atom of hydroxyl group in monosaccharide may interact with negatively charged oxygen at the surface (Singh and Mohan 2004). Liu and Laskowski, who studied the adsorption of dextrin at the lead oxide considered the exchange of saccharide with H^+ from surface hydroxyl groups as the most probable mechanism (Liu and Laskowski, 1989). Basing on results of spectroscopic analysis Zhang et al. have concluded that hydrogen bonding is the driving force in the adsorption of n-dodecyl- β -D-maltoside on alumina (Zhang et al. 2002).

This paper presents the results of kinetic and static study of fructose adsorption at the alumina/electrolyte interface using a radiolabeled compound (^{14}C -fructose). Beside the adsorption measurements, some complementary experiments, that is potentiometric titrations, electrokinetic measurements as well as Raman and FTIR spectra were also carried out.

Experimental

Materials

All the experiments were carried out using commercial nanoalumina from NanoTek (Nanophase Corporation, USA). The specific surface area of the alumina sample as determined by the BET method was $41.5 \text{ m}^2/\text{g}$. X-ray analysis has shown that the oxide has a crystallographic of $\gamma\text{-Al}_2\text{O}_3$ structure characterized in card 00-016-0394 with addition of $\gamma\text{-Al}_2\text{O}_3$ oxide characterized by card 00-004-0877 of International Centre for Diffraction Data. Barrett-Joyner-Halenda (BJH) volume analysis of the isotherm obtained by adsorption-desorption of nitrogen revealed that the volume of micropores was $0.16 \text{ cm}^3/\text{g}$ in the Al_2O_3 sample examined. Surface charge density of the studied sample of alumina/aqueous solution of NaCl as a function of pH shows that pH_{pzc} is equal to 7.9 but electrophoretic mobility measurements give $\text{pH}_{\text{iep}} = 8.5$. The values of surface charge were corrected of $8.5 \text{ } \mu\text{C}/\text{cm}^2$ to achieve $\text{CIP} = \text{pH}_{\text{pzc}}$. The presented value of pH_{pzc} is very close to the mean value of alumina $\text{pH}_{\text{pzc}} = 7.92$ and median $\text{pH}_{\text{pzc}} = 8.15$ (Kosmulski 2001). Adsorption experiments were carried out with radio-labelled fructose (ARC American Radiolabelled Chemical Inc., USA). Total activity and specific activity of the ^{14}C -fructose used were $250 \text{ } \mu\text{Ci}$ and 300 Ci/mol respectively.

Methods

The surface charge density at the alumina/electrolyte solution interface was determined by potentiometric titration of the oxide suspension. The measurement was carried out in a thermostated PTFE vessel, under nitrogen atmosphere free of CO_2 , at $25 \text{ } ^\circ\text{C}$. Measurements of pH were carried out using a PHM 240 Radiometer Research pH meter with K401 as a glass electrode and G202B as a reference calomel electrode. Potentiometric titration was carried out with use of automatic burette Dosimat 665 (Metrohm). The whole experiment was controlled by a computer software.

Potentiometric titration as well as electrokinetic measurements were carried out at three different concentrations: $1 \cdot 10^{-3}$ M, $1 \cdot 10^{-2}$ M and $1 \cdot 10^{-1}$ M of NaCl solutions. The initial concentrations of fructose were $1 \cdot 10^{-6}$ M, $1 \cdot 10^{-5}$ M, $1 \cdot 10^{-4}$ M, $1 \cdot 10^{-3}$ M. All the solutions were prepared with twice distilled water. All the reagents used for experiments were of analytical grade purity. The ζ potential of the alumina was determined by electrophoresis using a Zetasizer 3000 Standard (Malvern). The concentration of alumina in the electrolyte solution was 100 ppm. Before measurements the suspension of alumina was ultrasonicated. The adsorption density of fructose at the alumina/electrolyte solution interface was measured using radiotracer technique. Fructose solutions were labelled with ^{14}C isotope. The adsorption of D-fructose was studied by determining the changes in radioactivity of the solution with the use of potentiometric titration setup. A predetermined volume of the electrolyte solution (50 cm^3 0.001 M NaCl) was placed (at $25 \text{ }^\circ\text{C}$) in a PTFE vessel, to which 0.2 cm^3 HCl was then added. Inert atmosphere was provided by passing nitrogen over the solution. The solution of electrolyte of required ionic composition and concentration of D-glucose was then treated with a solution containing D-fructose labelled with ^{14}C . In order to determine the initial activity three samples of the solution ($100 \text{ }\mu\text{l}$ volume each) were taken as the zero samples. After equilibrium conditions were attained (constant temperature of $25 \text{ }^\circ\text{C}$ and pH of the solution) a weighed sample of the oxide (1 g) was added. A computer, controlling the process on the basis of pH-meter values, dosed successive portions of 0.1 M NaOH solution and determined the moment of taking the samples that should demonstrate the course of adsorption on the oxide surface. At that time a 0.5 cm^3 portion of the suspension was taken and the precipitate was centrifuged. Two $100 \text{ }\mu\text{l}$ samples of the centrifuged suspension were then taken and added to containers containing 3 cm^3 of liquid scintillator Insta Gel Plus (PerkinElmer Life And Analytical Sciences, Inc, USA). The pulses were then counted in a scintillation counter Beckman LS-5000DT (Beckman, USA). The adsorption of ions was studied at pH range 3 to 11. Calorimetric measurements were performed using a TAM Thermal Activity Monitor 2277 system micro-calorimeter from Thermometric, Sweden. A $200 \text{ }\mu\text{l}$ sample of 0.001 M solution of fructose was injected by means of a Hamilton syringe into a vessel containing a suspension of alumina (after equilibration of the solid/solution reactions). During the calorimetric experiments the ratio of fructose to alumina was identical as in the adsorption measurements. In order to confirm the presence of D-fructose adsorbed on the alumina surface DRIFT type and Raman spectra of the samples were recorded. The DRIFT spectra were taken with the use of a Perkin-Elmer FTIR 1725X spectrophotometer, and Raman spectra were recorded by means of a Raman microscope Via Reflex produced by Renishaw.

Results and discussion

Fructose adsorption kinetics

The studies of fructose adsorption kinetics following its addition to alumina suspension have shown that the changes of fructose concentration in the solution are accompanied by a change of pH thus leading to change in the structure of electric double layer (edl). The results of fructose adsorption kinetics on aluminium oxide surface were matched with the adsorption models (pseudo 1st order and pseudo 2nd order) to check which suits the best to the description of the process. The kinetics of adsorption proceeding according to the model of pseudo 1st order is described by Equation 1 and pseudo 2nd order by Equation 2 (Marczewski 2007; Rudzinski and Plazinski 2007):

$$\frac{dq_t}{dt} = k_1(q_1 - q_t) \quad (1)$$

$$\frac{dq_t}{dt} = k_2(q_2 - q_t)^2 \quad (2)$$

where: q_1 – amount of substance adsorbed in time t in the state of equilibrium, expressed in mol/m², conforming to a model of 1st order adsorption, q_2 – amount of substance adsorbed in time t in the state of equilibrium, expressed in mol/m², conforming to a model of 2nd order adsorption reaction, k_1 – rate constant of 1st order adsorption reaction, k_2 – rate constant of 2nd order adsorption reaction.

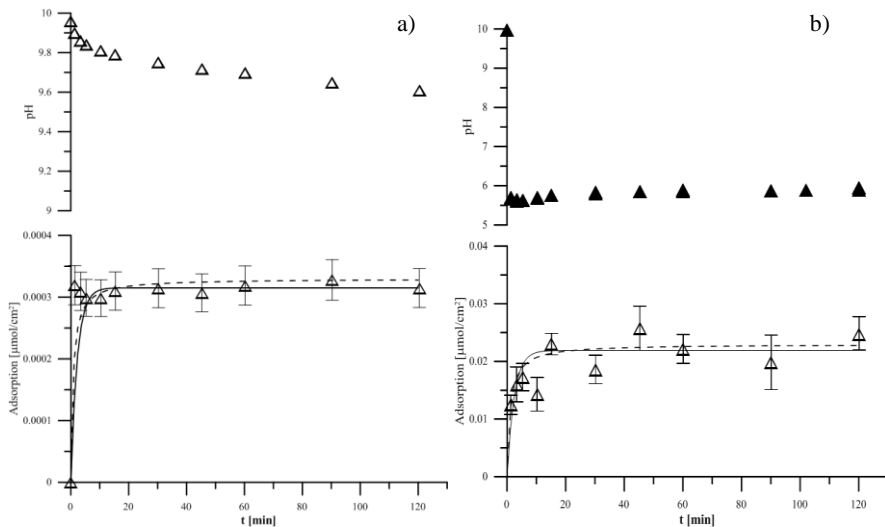


Fig. 1. Kinetics of fructose adsorption from solutions of initial concentration (a) $1 \cdot 10^{-6}$ M and (b) $1 \cdot 10^{-3}$ M

Figures 1a and 1b show the kinetics of fructose adsorption from solutions of initial concentration of $1 \cdot 10^{-6}$ and $1 \cdot 10^{-3}$ M, respectively. The continuous line represents the results of matching the model of 1st order, and the broken line – those for matching the model of 2nd order. The equation of pseudo 1st order or its integral form often referred to as Lagergen equation is often used for description of adsorption kinetics conforming to Langmuir model. Rudzinski and Plazinski (2007) have shown that both the Lagergen equation and the pseudo 2nd order equation may be used for description of adsorption on energetically heterogeneous surfaces. As can be seen the kinetics of fructose adsorption at Al_2O_3 /electrolyte solution interface sets rather quickly for the lowest concentration within initial several minutes. Because of experimental limitations (sample rotation) it was not possible to measure the adsorption in shorter time and to resolve the question which of the two models provides a better description of the process. In the case of the highest concentration $1 \cdot 10^{-3}$ M somewhat better fitting was obtained for the model of pseudo 2nd order. The results of fitting tests may be accounted for energetic surface heterogeneity of the oxide studied. We have also tested the fitting of equation describing the adsorption kinetics conforming to the model of intermolecular diffusion, but low degree of fitting was found for the data presented above. The kinetics of fructose adsorption and changes in pH were also studied after addition of a suitable amount of fructose to a suspension of Al_2O_3 (pH equilibrium was attained) so that the initial concentration of fructose was $1 \cdot 10^{-4}$ M. It has been observed that the process of adsorption sets very quickly within initial several minutes, whereas the decrease of pH proceeds much slower. This fact indicates that H^+ ions are not liberated due to fructose adsorption, since in such a case a rapid decrease of pH should be observed, followed by an increase owing to further adsorption of H^+ ions on surface hydroxyl ions of the oxide.

Fructose adsorption as a function of pH

Fructose is a monosaccharide of very weak acidic properties and negative logarithm of dissociation constant $\text{p}K_a = 12.6$. The share of fructose forms in the pH function shows that undissociated form of fructose would dominate in the pH range tested. Former studies by Singh and Mohan (2004) have shown that the adsorption of fructose increases with increasing pH. The following mechanisms of fructose adsorption have been proposed for explaining this relationship: exchange of fructose to water molecule in the group $=\text{AlOH}_2^+$ and creation of hydrogen bond between the monosaccharide and hydroxyl group of the oxide surface. The proposed mechanism of exchange of water molecule for fructose on the $=\text{AlOH}_2^+$ group should lead to decrease of monosaccharide adsorption with increasing pH as a consequence of decrease of concentration of the $=\text{AlOH}_2^+$ groups.

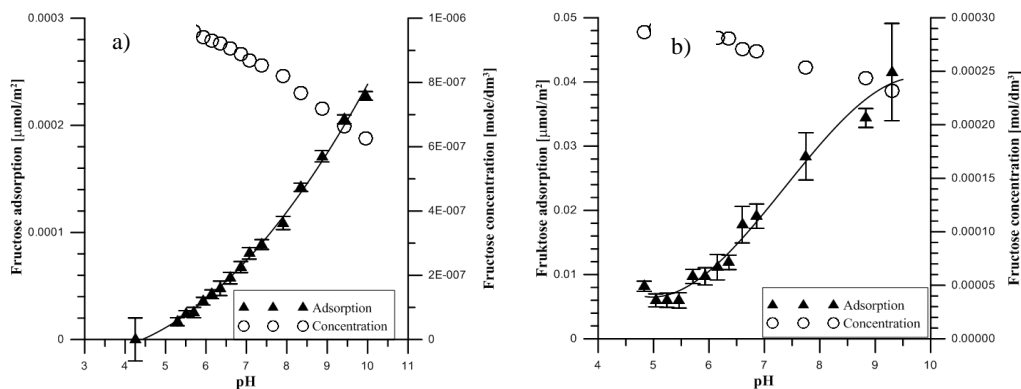


Fig. 2. The results of fructose adsorption as a function of pH for initial concentrations. (a) $1 \cdot 10^{-6}$ M and (b) $3 \cdot 10^{-4}$ M

The results of fructose adsorption as a function of pH have been shown in Fig. 2a and 2b for initial concentrations of $1 \cdot 10^{-6}$ M and $3 \cdot 10^{-4}$ M. As can be seen in Fig. 2a and 2b the adsorption of fructose increases with increasing pH. Such course of adsorption curve is characteristic for cation adsorption at the interface between metal oxide and electrolyte solution. For multivalent cations the increase of adsorption is sharper by the so-called adsorption edge ranging 1–2 pH units. Since the acidic properties of fructose are weak, such a mechanism of adsorption cannot explain the observed relationships. Another, more probable mechanism is an adsorption on groups, the concentration of which increases with increasing pH; the concentration of $=\text{AlOH}$ increases up to pH_{pzc} , then it decreases and concentration of $=\text{AlO}^-$ starts to increase. Assuming, that fructose is adsorbed on the groups by means of hydrogen bonds, such an interaction increases the probability that the mechanism of adsorption is responsible for the increase of fructose adsorption with increasing pH. Still another mechanism of fructose adsorption on aluminium oxide surface, that might be taken into consideration, is the reaction of formation of a surface complex similar to that proposed by Liu and Laskowski (1989) who described the interaction of dextrin with the surface of lead hydroxide and by Weissenborn and Pradu (1995) and Ravishankar et al. (1995) in their studies of starch adsorption on hematite. According to their study adsorption of polysaccharides lead to release of hydrogen ions. However the proposed in these papers reaction of adsorption the charge balance is violated and according to this reaction for low initial concentration of fructose, its concentration in the solution should decrease from 100 % to almost 0 % due to its adsorption similarly to the metal ions adsorption at metal oxide electrolyte interface. So the another mechanism of the adsorption should be considered. The $=\text{AlOH}_2^+$ structure formed corresponds largely to the structure of water molecule coordinated on aluminium ions, so the monosaccharide molecules present in the suspension may be coordinated on surface aluminium atoms of Al_2O_3 by replacing water molecules in its coordination sphere. According to Hidber et al. (1997) the formation of a surface complex does not take

place if the pH of the suspension is much lower than pK_a of the ligand. Under such conditions the ligand is strongly bound with proton. The studies of D-fructose adsorption were carried out at pH 4–11 where pK_a of fructose is 12.03. Hence in the range under study $pH < pK_a$, and the nature of adsorption is different than formation of surface complexes. This fact was confirmed in the study on effect of concentration of basic electrolyte (NaCl) on fructose adsorption on aluminium oxide, as shown in Fig. 3. As can be seen, even a 100-fold increase of electrolyte concentration gave only a slight decrease of fructose adsorption. It means that the nature of fructose adsorption is not the ion exchange, since in such a case the effect of concentration on adsorption of fructose should be stronger because of competition to adsorption sites. The observed small decrease of adsorption may result from the smaller activity in the solution or decrease of the number of adsorption sites on the oxide surface as a consequence of reaction of Na^+ ions with surface hydroxyl groups.

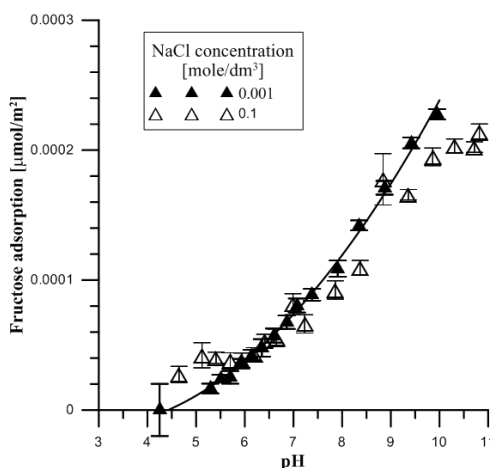


Fig. 3. The study on effect of concentration of basic electrolyte (NaCl) on fructose adsorption on aluminium oxide

Isotherm of fructose adsorption at the $Al_2O_3/NaCl$ solution interface

A fructose adsorption isotherm as a function of equilibrium concentration shown in Fig. 4. in the system $\log(\text{adsorption})$ vs. $\log(\text{concentration})$ (the so-called Kurbatov plot) is linear in the range of low concentrations. The slope of linear sections of the diagram varies from about 1 for $pH = 6$ to 0.86 for $pH = 10$. The slope equal 1 is characteristic for adsorption under conditions where the Langmuir model of adsorption is obeyed. Lower values of adsorption coefficient are characteristic for adsorption on surfaces with energetically heterogeneous adsorption sites. In the studies on corrosion inhibition of an aluminium pigment Muller (2002) found the minimum and maximum surface areas occupied by a fructose molecule as 0.32 nm^2 and 0.60 nm^2 , respectively. Approximate calculations show that covering with a

monomolecular layer of fructose would give maximum adsorption densities between $5.19 \mu\text{mol}/\text{m}^2$ and $2.77 \mu\text{mol}/\text{m}^2$. The values of adsorption densities shown in Fig. 4. are therefore several dozen times lower than the maximum expected. It is therefore probable that the adsorption of fructose does not engage all the unionized hydroxyl groups.

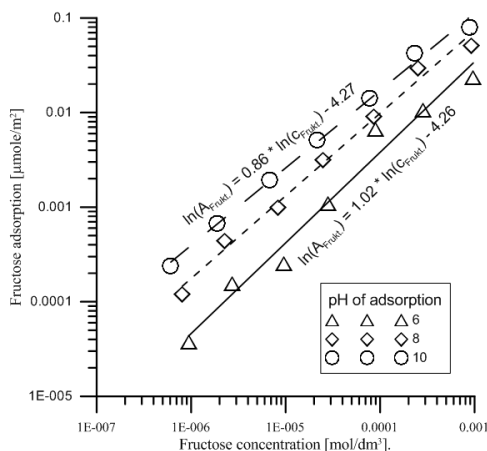


Fig. 4. A fructose adsorption isotherm as a function of equilibrium concentration

Calorimetric measurements of the fructose adsorption

Measurements of heat of fructose adsorption at the interface of aluminium oxide/0.001 M solution of NaCl carried out with the use of Thermal Activity Monitor 2277 microcalorimeter showed that addition of 200 μl fructose to 2 cm^3 suspension of 0.001 M NaCl containing 0.08 g Al_2O_3 liberated 2.426 mJ of heat. As the conditions of calorimetric measurement (ratio of adsorbent surface area to the volume of solution) were identical as in the case of adsorption measurement at initial fructose concentration 0.001 M, 0.22 μmol of fructose was adsorbed, hence the heat of adsorption was 10.8 kJ/mol, which is characteristic for the hydrogen bond.

Effect of fructose adsorption on density of surface charge and zeta potential

The relationships between the surface charge density and pH in the system: aluminium oxide/fructose solution, presented in Fig. 5. show, that the presence of fructose in the system of Al_2O_3 increases the density of surface charge at pH range 5 – 6. Since at that pH range the adsorption of fructose is rather small, this fact may be due to indirect effect of fructose on interaction of water molecules with surface hydroxyl groups via the hydrogen bond. Such a mechanism of charge variations was strongly supported by the results of numeric simulation of interaction between fructose and water molecules presented by Pomata et al. (2009), which revealed the decrease of mobility of water molecules owing to hydrogen bond interaction with

fructose. Another support was provided by Li et al. (2005), who measured the viscosity of aluminium oxide suspension containing fructose and mobility of water molecules in that system. It has been shown that the presence of fructose in the system decreases the viscosity of the suspension and increases the mobility of water molecules owing to release of water from the surface of alumina particles. That provides a possibility to increase the number of H^+ ions interacting with $=AlOH$ and $=AlO^-$ groups (Hiemstra et al., 1996). The relationship between zeta potential and pH in the presence of fructose, as shown in Fig. 6., is at lower pH values slightly higher than in the case of 0.001 M NaCl solution containing no fructose. The effect conforms with increase of surface charge density in the pH range 5–6. As it was mentioned above, in the case of anion adsorption one might expect an increase of surface charge density depending on the amount of fructose adsorbed.

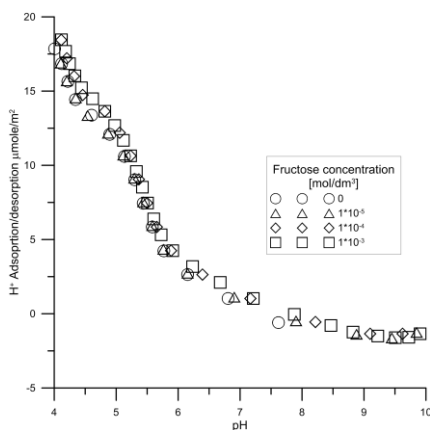


Fig. 5. The surface charge density and pH in the system: aluminium oxide/fructose solution

This effect cannot be seen in Fig. 5, since in this pH range fructose occurs in solution in undissociated form. Besides, the adsorption of anions decreases with increasing pH. No liberation of hydrogen cations, observed by Liu and Laskowski (1989), can also be seen in the adsorption of dextrin on aluminium hydroxide. Assuming, that the adsorption of fructose at alumina/electrolyte solution interface proceeds according to the mechanism proposed by Liu and Laskowski (1989), for initial fructose concentration of $1 \cdot 10^{-3}$ M about $1 \cdot 10^{-4}$ M of H^+ cations should be liberated, hence the decrease of pH should be noticeable. Since the observed changes in charge density and zeta potential are small but univocal, the most probable mechanism may consist in adsorption of fructose on surface of Al_2O_3 by interaction of hydrogen bridge with hydroxyl groups conforming to the mechanism 2 as proposed by Singh and Mohan (2004). However, above pH_{pzc} of aluminium oxide the surface concentration of hydroxyl groups decreases and it becomes necessary to assume that the adsorption can result as a consequence of interaction of hydrogen from the

hydroxyl group of fructose with negatively charged oxygen from surface group. This assumption has been confirmed by measurements of kinetics of pH changes due to adsorption of fructose.

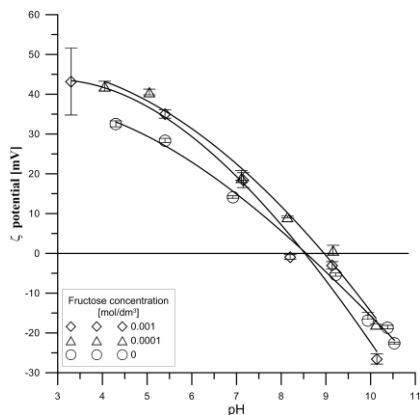


Fig. 6. The zeta potential and pH in the presence of fructose

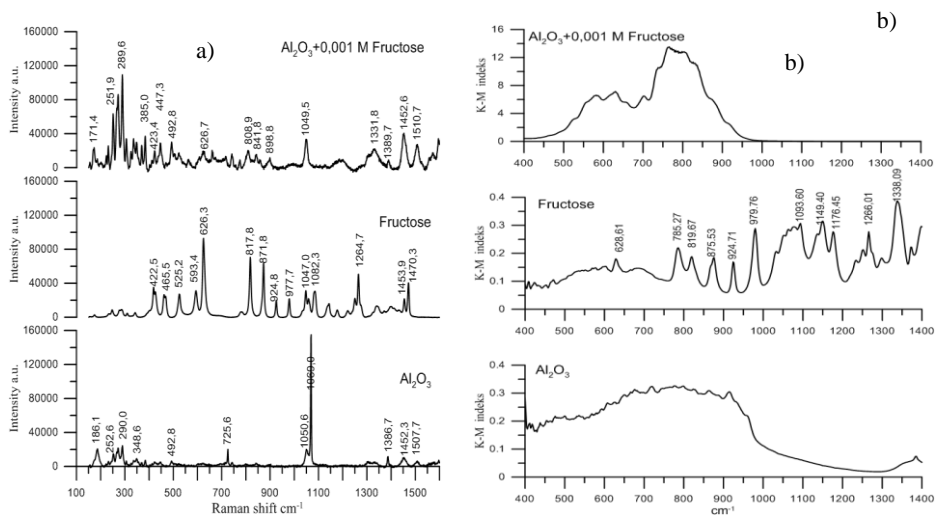


Fig. 7. (a) Raman spectra of Al_2O_3 , fructose and fructose adsorbed on Al_2O_3 from (a) 0.001 M solution and (b) DRIFT spectra

Results of Raman and FTIR spectrometric study

Figure 7a shows a comparison of Raman spectra of Al_2O_3 , fructose and fructose adsorbed on Al_2O_3 from a 0.001 M solution. It is seen that the surface of the sample under study contains functional groups characteristic for pure Al_2O_3 (in the range of wave numbers $375,788\text{ cm}^{-1}$; $405,391\text{ cm}^{-1}$; $420,541\text{ cm}^{-1}$; $437,815\text{ cm}^{-1}$), but also unidentified groups probably due to surface impurities. Particularly high peak has been recorded at the wave number of $1069,02\text{ cm}^{-1}$. A comparison of fructose

spectrum with that obtained for Al_2O_3 containing adsorbed fructose shows that the latter contains a number of bands characteristic for fructose e.g. 626.7 cm^{-1} (Soderholm et al., 1999), that may be accounted for its presence on the oxide surface.

The DRIFT spectra obtained for these samples are shown in Fig. 7b. In this case the samples of Al_2O_3 with adsorbed fructose did not give separate peaks for individual vibrations, but only a broad band in the range of $500\text{--}950\text{ cm}^{-1}$. Nevertheless, the measurements have shown the presence of fructose, since the peaks 787.27 cm^{-1} ($\tau\text{CO}+\delta\text{CCO}+\delta\text{CCH}$); 819.67 cm^{-1} (δCH); 875.53 cm^{-1} ($\nu\text{CC}+\delta\text{CCH}+\delta\text{CH}$) and 924.71 cm^{-1} ($\nu\text{CO}+\delta\text{CCH}+\nu_{\text{asy}}$ (pyranose ring)) (Medhat et al., 2006) may be a cause of a complex peak observed for the sample containing adsorbed fructose in the range $700\text{--}950\text{ cm}^{-1}$.

Conclusions

The kinetic studies of fructose adsorption at the alumina/aqueous electrolyte interface indicates that equilibrium of adsorption is settled in a short time and may be described in terms of equations of pseudo 2nd order. Adsorption of fructose at interface aluminium oxide/electrolyte solution increases with increasing pH. However, this relationship is not connected with anion adsorption, but is result of interaction of fructose with hydroxyl groups and negatively charged oxyl groups, the concentration of which increases with increasing pH. Measurements of heat of fructose adsorption at the interface of aluminium oxide/0.001 M solution of NaCl shows that the energy of adsorption is comparable to energy of the hydrogen bonds. Hence, the hydrogen bonding is the most probable mechanism of interaction of fructose with the surface. Adsorption of fructose provokes slight changes in surface charge density and zeta potential, probably due to interaction of fructose with water molecules in the bulk of solution.

Acknowledgements

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