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Adsorption of 1,2-dihydroxyanthraquinone on silica surface

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The immobilization of alizarin on the surface of porous and nonporous silicas by adsorption from aprotonic and protoactive solvents has been investigated. The nature of reagent binding with the silica surface is discussed. The dissociation constant of the immobilized reagent has been determined. The possibility of modified sorbent application in analytical practice has been examined.

Изучена адсорбция ализарина из апротонных и протоактивных растворителей на поверхности пористого и непористого силикагелей. Обсуждена природа закрепления реагента на поверхности силикагелей. Определена константа диссоциации иммобилизованного ализарина. Установлена возможность использования модифицированного ализарином силикагеля в аналитической практике.

Recently, a considerable attention focused on the development of modified sorbents for sorption-spectroscopic and visual determination of metal ions in different objects [1]. Ion-exchange resins, polyvinyl chloride membranes and fibres are widely used as such solid matrices [2–4]. The application of high-dispersion silicas offers some distinct advantages over the using of organic polymer supports: a short equilibration time an excellent swelling resistance in different solvents, the easiness of surface modification with analytical reagent by adsorption [3]. The preparation of modified silicas *via* reagent adsorption is rather simple, and their chemico-analytical properties do not yield to those of sorbents with covalently grafted reagents [5]. Simultaneously, the use of specific chromophor reagents as modificators permits to raise the selectivity and sensitivity of determination. 1,2-Dihydroxyanthraquinone (Alizarin, Aliz) is known to be an effective chelating reagent for determination of some polyvalent metals [6]. As far as we know, no modification of silica by Aliz adsorption has been reported.

In the present work, the adsorption of Aliz from aqueous ethanol and toluene solutions onto silica surface and the protolytical and chelating properties of immobilized reagent have been studied.

Water was purified according to [7]. Methanol was purified by sodium metal. Porous silicas Silpearl UV 250 (SP) and silica gel L 40-100 (SG) for chromatography (Chemapol, Prague, Czech Republic) were digested in HCl (1:1), washed with purified water and dried at 80°C for 8 h. Non-porous highly dispersed silica Silics (Kalush, Ukraine; specific surface area $S = 300\ m^2 \cdot g^{-1}$) was used as received. Alizarin and Alizarin Red S monohydrate (Aliz S) (Merck, Germany) were recrystallized from ethanol and water respectively [6]. Standard phosphate buffer solutions with pH 1.68÷7.95 (the phosphate concenration 0.05 M) (Merck, Germany) were used. All chemicals used were of analytical reagent grade. Solutions of Aliz in toluene, ethanol, and aqueous solution of Aliz S were prepared by dissolving the appropriate amounts of substances. Standard solutions of $Al(NO_3)_3$ (0.01 M) and $ZrOCl_2$ (0.1 M) were prepared by dissolving $Al(NO_3)_3{\cdot}9H_2O$ in 0.1 M nitric acid and $ZrOCl_2{\cdot}8H_2O$ in 1.0 M hydrochloric acid, respectively, and then diluted as required. The amounts of Al(III) and Zr(IV) in solution after adsorption were controlled spectrophotometrically with Aliz-S [6].

IR spectra of Silics with adsorbed Aliz were recorded using a UR-20 (Carl Zeiss, Jena, Germany), spectrofotometer, samples being prepared as thin films between KBr windows. The reflectance spectra of modified sorbents (Aliz-SG), absorbance spectra of Aliz-SG suspensions (against pure silica suspension in the cell $l = 3$ mm) and Aliz solution were recorded using an UV/Vis spectrophotometer Specord M-40 (Carl Zeiss Jena, Germany). A Model EV-74 potentiometer with a glass electrode was used for pH measurements.

The batch technique has been used to study the Aliz adsorption and desorption. The adsorption from toluene and aqueous ethanol (1:1) solutions was examined as follows. The sorbent (0.02–0.50 g) was stirred mechanically with 5–10 ml of Aliz solution at initial concentration (C, M) and fixed pH (aqueous ethanol solution) until the equilibrium was reached (2–15 min and ~2 h, respectively). Aqueous ethanol solution after sorbent separation was acidified to pH 2. The residual Aliz in solutions ($[C]$, M) was determined spectrophotometrically by their own absorbance at 425 nm and 435 nm, respectively, according to calibration graph:

$$A = 4.07 \cdot 10^3\, C(M)(mol \cdot l^{-1}). \qquad (1)$$

The content of Aliz adsorbed on the surface was calculated according to the equation:

$$a = (C - [C]) \cdot V/1000m(mol \cdot g^{-1}), \qquad (2)$$

where V is the solution volume, ml; m, the sorbent mass, g. The desorption of Aliz from the surface was studied as follows. The weighed amount of modified sorbent (0.02 g) at different surface reagent content was stirred for 10 min with 10 ml of agueous solutions (pH = 0–7). The necessary pH value was adjusted by addition of HCl or KOH and controlled with pH-meter. The concentration of Aliz desorbed into solution was determined as was mentioned above. The modified sorbents for IR-measurements were prepared as follows. The Silics was dried in vacuum at 341 K for 10 h. The sorbent (0.1 g) was stirred for 5 min with 5 ml of toluene or methanol solutions that contained $2.5{\cdot}10^{-4}$ and $5.0{\cdot}10^{-4}$ $mol{\cdot}l^{-1}$ of Aliz. The content of adsorbed reagent (a, 10^{-6} $mol{\cdot}g^{-1}$) was 1.25 and 2.5, respectively.

The dissociation constant of Aliz in solution was determined as follows. A 0.2 ml aliquot of $1{\cdot}10^{-3}$ $mol{\cdot}l^{-1}$ ethanolic reagent solution, 2.0 ml of buffer solutions (pH 1.68, 4.75, 6.86), 2.5 ml of 2.0 $mol{\cdot}l^{-1}$ KCl (to create constant ionic strength of 0.5) and ethanol to obtain its 10, 20, and 50 % content were placed into a standard flask. Then water was added to total volume of 10 ml. The absorbance of mixtures was measured at 425 nm. The pH values of aqueous ethanol mixtures (pH_ω) were controlled using pH-meter. The pH dependence of phosphate buffer solutions on ethanol concentration was found to be expressed as:

$$pH_0 = pH_\omega - 0.028\omega, \qquad (3)$$

where pH_0, pH_ω are pH values at 0 and ω (%) ethanol concentration, respectively. The Aliz dissociation constant in aqueous solution was calculated as described in [8] using equation:

$$K = \frac{([H^+]_1 - [H^+]_3) \cdot (A_1 \cdot [H^+]_1 - A_2 \cdot [H^+]_2) - ([H^+]_1 - [H^+]_2) \cdot (A_1 \cdot [H^+]_1 - A_2 \cdot [H^+]_3)}{(A_1 - A_3) \cdot ([H^+]_1 - [H^+]_2) - (A_1 - A_2) \cdot ([H^+]_1 - [H^+]_2)}, \qquad (4)$$

where A_1, A_2, A_3 are absorbances of Aliz solution at pH 1.68, 4.75, 6.86, respectively: $[H^+]$ was calculated according to equation (3) using experimental data on pH_ω.

The conditional dissociation constant (K^*) of Aliz immobilized on SG was determined as follows. Several aqueous mixtures (10 ml each) with constant ionic strength ($\mu = 0.5$) were buffered to pH 1.68, 4.75 or 6.86 and stirred mechanically with modified SG (0.2 g, $a = 7.1{\cdot}10^{-6}$ $mol{\cdot}g^{-1}$) until equilibrium (20 min). The sorbents were separated, dried and their reflection factors at

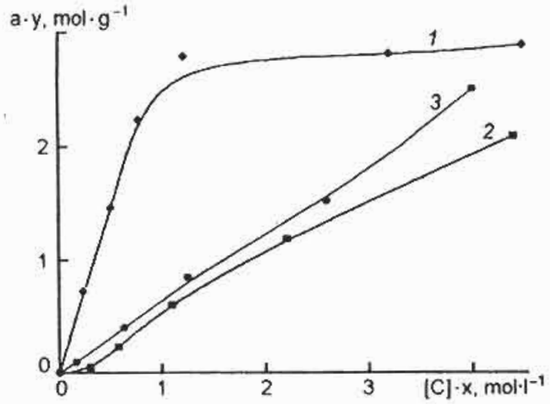

Fig. 1. Isotherms of Aliz adsorption onto SG from aqueous ethanol (1:1) at pH = 3.6 (*1*), from toluene onto SG (*2*) and Silpearl (*3*); x — 10^5 (*1*), 10^4 (*2*, *3*), y — 10^7 (*1*), 10^5 (*2*, *3*). $T = 295.0 \pm 0.5$ K.

$\lambda = 425$ nm were measured. The dissociation constant was calculated as described in [8] using equation (4), where A_1, A_2, A_3 were reflection factors of Aliz-SG at pH 1.68, 4.75, 6.86, respectively.

The pH dependence of Aliz adsorption from aqueous-ethanol solutions was studied. The reagent recovery was found to decrease with increasing positive charge of silica surface ($SiOH_2^+$ site prevails at pH<3 [9]). The experimental curve reached the saturation at pH≥3.6. The Aliz adsorption isoterm on SG surface from aqueous ethanol solutions is presented in Fig. 1 (curve 1). *L*-type of isotherm and difficult removing of Aliz from silica surface by ethanol and chloroform testify to a rather strong binding of reagent with SG surface [10]. The maximum adsorption capacity of porous SG with respect to Aliz ($4 \cdot 10^{-7}$ mol·g^{-1}) is 3.5 times more than that of nonporous Silics. Taking into account similar specific surface areas of these silica gels, we have supposed that a considerable Aliz amount penetrates into pores at such reagent immobilization. The analytical application of silica with Aliz adsorbed from aqueous ethanol solution is limited because of low adsorption capacity.

The adsorption of analytical reagents from non-polar organic solvents is known to be an effective method of silica modification [5]. Aliz adsorption onto SG from toluene, hexane and chloroform solutions has been studied. The best reagent adsorption was observed in the case of toluene. Kinetic experiments have shown that the equilibrium of Aliz adsorption from toluene solution is reached in 30 s. Isotherms of Aliz adsorption onto SG and Silpearl (Fig. 1, curves 2 and 3) can be ascribed to *S*-type which is typical of the adsorption of polynuclear aromatic compounds with several functional groups from non-polar solvents onto polar sorbents [10]. The *S*-form of the isotherms shows that adsorption becomes easier as the concentration rises. That can be because the reagent molecules exhibit a moderate intermolecular attraction causing it to be packed themselves vertically in regular array in the adsorbed layer. This type of isotherm also indicates a tendency for large adsorbed molecules to associate rather than to remain as isolated units.

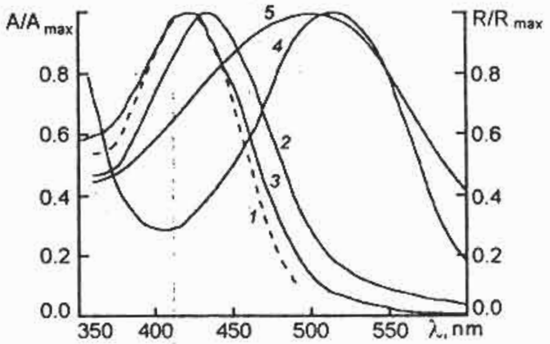

Fig. 2. Standardized adsorption spectra of toluene *1*), ethanol (*2*), aqueous ethanol (1:1) solutions of Aliz at pH 2 (*3*), 9 (*4*), and the reflectance spectrum of Aliz-SG (*5*).

Taking into consideration the fact that there is no strong competition from the toluene molecules, the non-coplanar Aliz fixation on surface at monolayer formation can be supposed. The absence of plateaus on curves 2 and 3 (Fig. 1) shows that the second molecular layer can be formed on the sorbent surface simultaneously with the completing of the first one [11]. The second layer formation may take place due to the Aliz-Aliz molecular interaction. To check this hypothesis, the absorption spectra of Aliz in aqueous ethanol and toluene solutions and the reflectance spectra of modified silicas with different Aliz content were compared. The spectra show that the polarizing effect of silica surface on β-OH-group of Aliz in the monolayer ($a < 1 \cdot 10^{-6}$ mol·g^{-1}) is stronger than that of the protoactive solvents in solution, in particular, ethanol, (Fig. 2). However, this OH-group is not dissociate completely. The reflectance spectra (Fig. 3) prove that the surface polarizing influence becomes weaker as the Aliz content on silica surface increases. That also confirms the polymer Aliz layer formation under these conditions [11].

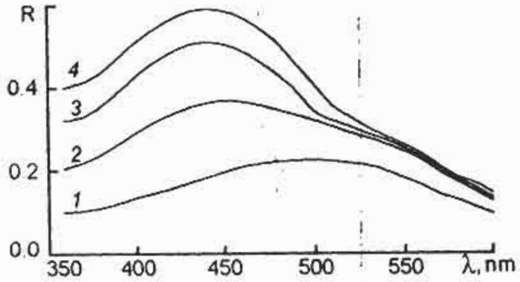

Fig. 3. Reflectance spectra of SG with adsorbed Aliz at different reagent content on the surface; 10^{-6} mol·g^{-1}, 0.95 (*1*), 4.03 (*2*), 8.37 (*3*), 15.3 (*4*).

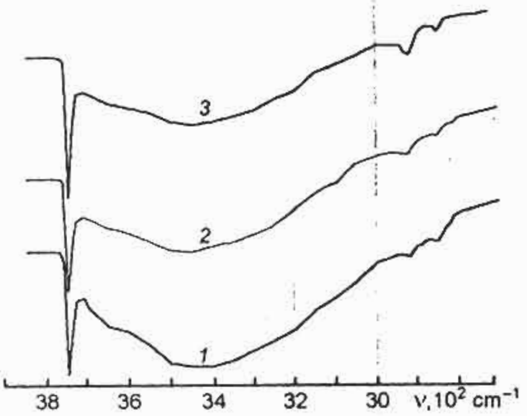

Fig. 4. IR spectra of nonmodified (*1*) and modified (*2*, *3*) Silics with different Aliz content on the surface; 10^{-6} mol·g^{-1}, 1.25 (*2*), 2.5 (*3*).

IR spectra shown in Fig. 4 indicate that absorption band at 3749 cm^{-1} which belongs to a valence vibration of singular surface OH-groups [12], becomes more intense as the Aliz surface content increases. Simultaneously, a significant weakening of absorption band at 3200–3600 cm^{-1} corresponding to the stretching vibration of the *hydrogen-bonded (vicinal)* silanol groups, is observed. This indicates that the vicinal silanol groups are involved into the Aliz fixation on the surface. The maximum adsorption capacity of SG and Silpearl was experimentally found to be $2.1 \cdot 10^{-5}$ and $2.5 \cdot 10^{-5}$ mol·g^{-1} respectively. However, the capacity of the nonporous Silics was approximately 3 times less than that of porous silicas. This fact confirms the supposition on the role of pores in Aliz adsorption. The stability of modified sorbents in acidic medium was examined. The desorption of Aliz from the surface into aqueous solution (pH = 0–6) was less than 5–8 % for sorbents with $a \geq 5 \cdot 10^{-6}$ mol·g^{-1}. Such sorbents are suitable for the analytical use within this pH range.

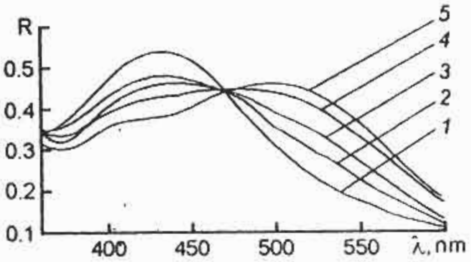

Fig. 5. Reflectance spectra of Aliz-SG with Zr adsorbed. Initial concentration of $ZrOCl_2$, 0 (*1*), 0.2 (*2*), 1.6 (*3*), 3.2 (*4*), (*5*) — $8.0 \cdot 10^{-5}$ mol·l^{-1}; $a = 5 \cdot 10^{-5}$ mol·g^{-1}.

Immobilization of analytical reagents on silica surface is known to cause alteration of their protolytical properties [13]. The conditional dissociation constant of adsorbed Aliz determined using the diffusion reflectance spectroscopy amounted $pK^* = 4.4 \pm 0.1$ ($n = 3$, $P = 0.95$). Since the values of Aliz dissociation constant in aqueous solution given by different authors are rather contradictory [14], we have determined this constant as well ($pK = 5.9 \pm 0.1$; $n = 3$, $P = 0.95$). The significant increasing of Aliz dissociation constants at its fixation on the silica surface is probably explained by the surface effect.

It is known [6], that Aliz forms coloured complexes with Al(III) and Zr(IV). We have studied the possibility to use Aliz-SG for preconcentration and determination of these metal ions. The pH dependence of Al(III) adsorption from aqueous solution onto Aliz-SG evidences that the quantitative recovery is observed at pH≥3. However, the reproducible results have not been obtained because Al(III) forms stable hydroxocomplexes under these conditions. Zr(IV) is known to *interact with Aliz at pH 0–1* [6]. Under these conditions, the adsorption of Zr(IV) onto Aliz-SG was found to be rapid and quantitative. The reflectance spectra of Aliz-SG with adsorbed Zr(IV) shown in Fig. 5 indicate the possibility of Aliz-SG application for the adsorption-spectroscopic as well as for visual test determination of Zr(IV).

Thus, the Aliz immobilization onto silica surface by adsorption from toluene was performed. The study of Aliz binding nature with SG surface has shown the non-coplanar reagent grafting at the step of monolayer formation. The second layer is formed through the Aliz-Aliz molecular interaction. It was found that the immobilization of Aliz strengthens its acid properties. The sorbent with Aliz adsorbed was found to be stable within a rather wide pH range. This silica was shown to be suitable for Zr(IV) determination by using of diffusion reflectance spectroscopy.

References

1. R.E.Clement, G.A.Eiceman, C.J.Koester, *Anal. Chem., Appl. Rev.* **67**, 221R (1995).
2. Chi-Chung Wan, S.Chiang, A.Corsini, *Anal. Chem.*, **57**, 719 (1985).
3. M.A.Marshall, H.A.Mottola, *Anal. Chem.*, **57**, 729 (1985).
4. P.Battistoni, S.Bompadre, G.Fava, G.Gobbi, *Talanta*, **30**, 15 (1983).
5. O.A.Zaporozhets, O.M.Gawer, V.V.Sukhan, *Russ. Chem. Rev.* **66**, 637 (1997).
6. Z.Marczenko, Colometric Determination of Elements, Wydawnictwo Naukowo-Techniczne, Warszawa (1968) [in Polish].
7. Methods of Analysis of Pure Chemical Reagents, Khimia, Moscow (1984) [in Russsian].
8. N.P.Komar, *Uchen. Zapiski, Kharkov Gos. Univ., Trudy Khim. Fak. i NII Khimii*, **8**, 57 (1951).
9. R.K.Iler, The Chemistry of Silica, New York: Wiley-Interscience (1979).
10. C.H.Giles, T.H.McEwan, S.N.Nakhwa, D.Smith, *J. Chem. Soc.*, **10**, 3973 (1960).
11. A.N.Terenin, Photonics of Molecules of Dayes and Related Organic Compounds, Nauka, Leningrad (1967) [in Russian].
12. A.V.Kiselev, V.I.Lygin, Infrared Spectra of Surface Compounds, Nauka, Moscow (1972) [in Russian].
13. G.V.Lisichkin, Use of Modified Silica in Adsorption, Catalysis, and Chromatography, Khimia, Moscow (1986) [in Russian].
14. Stability Constants of Metal-ion Complexes: Part B. Organic ligands (Ed. D.D.Perrin), Pergamon Press, Oxford-N.Y.-Toronto-Sydney-Paris-Frankfurt (1988).

Адсорбція 1,2-дигідроксиантрахінону на поверхні силікагелю

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Досліджено адсорбцію алізарину з апротонних та протоактивних розчинників на поверхні пористого та непористого силікагелей. Обговорено природу закріплення реагенту на поверхні силікагелей. Визначено константу дисоціації іммобілізованого алізарину. Встановлено можливість застосування модифікованого алізарином силікагелю в аналітичній практиці.