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SUPRAMOLECULAR COMPLEXES OF IONITES WITH ORGANIC SUBSTRATES

Abstract. In the present work, the general laws of the interaction of aromatic and heterocyclic acids with the anionite AV-17-8 have been studied by IR spectroscopy. Adsorption was studied under static conditions. The nature of the interaction was judged by the appearance of new bands, the shift of their maxima and the change in intensity on the spectrograms of fresh and spent ionite samples. IR absorption spectra of the freshly prepared anion exchanger in the OH form were obtained and after mixing it with organic acids. Based on the data on the IR spectra of the anionite AV-17-8 after adsorption of carboxylic acids, various aggregate supramolecular complexes of adsorbed molecules with active centers of the ion-exchange resin are proposed. It has been shown that the molecules with pyridine derivative substituents have the best tendency to adsorb, owing to the high degree of intramolecular resonance and the formation of anions upon adsorption on the anion exchanger. It was found that acid adsorption is carried out due to the formation of a hydrogen bond with hydroxyl groups located on the surface of the adsorbent. In the anionite spectra after the adsorption of organic acids, absorption bands corresponding to symmetric and antisymmetric valence vibrations of the carboxylate of anions were observed.

Keywords:adsorption, carboxylic acids,anion exchange.

Supramolecular chemistry studies the associates of two or more particles held together by intermolecular forces. It can be said that supermolecules refer to molecules and intermolecular bonds, as molecules belong to atoms and covalent bonds [1]. From these positions, it seems to us, it is more convenient to consider ion exchangers, which are increasingly used in the purification of waste water and flue gases from harmful impurities. In addition, they are increasingly used as heterogeneous catalysts in organic synthesis.However, the mechanism of intermolecular interaction between adsorbates and active groups of ion exchangers has not been sufficiently studied[2-11]. The knowledge of the laws governing the formation of associates, their structure and intermolecular forces, which hold together different molecules and active surface centers of adsorbents, will allow them to be used more efficiently and selectively for these purposes.

The present work is devoted to the study of the adsorption of organic acids on the anioniteAV-17-8 in the OH form by IR spectroscopy, the formation of intermolecular aggregate associates of adsorbed molecules with active ionite centers.

Experimental part

In the work, commercial ion exchanger with a grain diameter of 0.3-0.5 mmhas been used, which was conditioned and transferred to the OH-form by the method [12]. The static exchange capacity of 0.1 N hydrochloric acid solution was 4.2 mg-eq / g.

The adsorption was carried out in a glass reactor equipped with a reflux condenser, with a temperature of 25 to 75 ° C for 1-2 hours and an adsorbate: ionite: water ratio of 1: 2: 8. After treatment, the ion exchanger was filtered, washed with water, dried in air in a drying oven at 30-50 ° C., then kept in a desiccator over $P_2O_5$for 24 hours, tableted with pre-recrystallized and dried up to the complete disappearance of KBr bands and recordedspectra on thespectrometer Impact 410 (USA) in the field of 4000-400 cm^{-1}.

Results and their discussion

We first studied the adsorption of pyridinecarboxylic and aromatic acids on the anioniteAV-17-8 in the OH form.

Pyridinecarboxylic acids and their derivatives are part of the waste water of coke production, in particular, in the production of vitamins and antituberculosis drugs. Therefore, a study of the mechanism of their sorption is of interest both from the point of view of environmental protection and the capture of valuable raw materials.

In the spectrum of fresh ionite (1), a number of bands in the region of 1380-1500 cm^{-1}pertain to the deformation vibrations of the CH_2, CH_3 groups and the skeletal vibration of the benzene ring. The wide band in the field of 1600-1700 cm^{-1}corresponds to the deformation vibration of the OH groups of water [13-18].

The spectra of nicotinic (2), isonicotinic (3), benzoic (7) acids and the products of their interaction with anionite (4), (5) and (6), respectively, are shown in the figure.

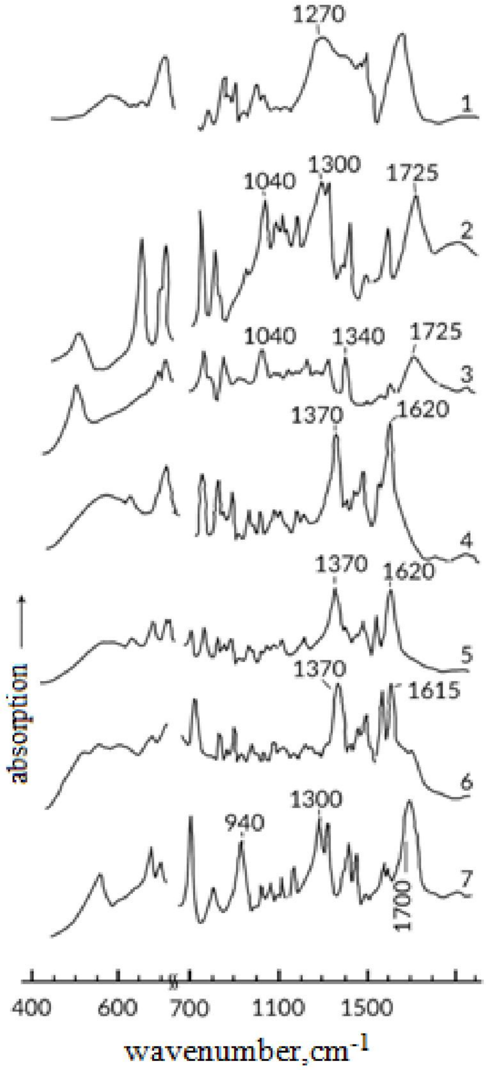
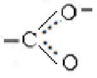


Figure - IR adsorption spectra of the anioniteAV-17-8 in the OH form (1) of nicotinic (2), isonicotinic (3), benzoic (7) acids and their interaction products with anionite (4, 5, 6, respectively)

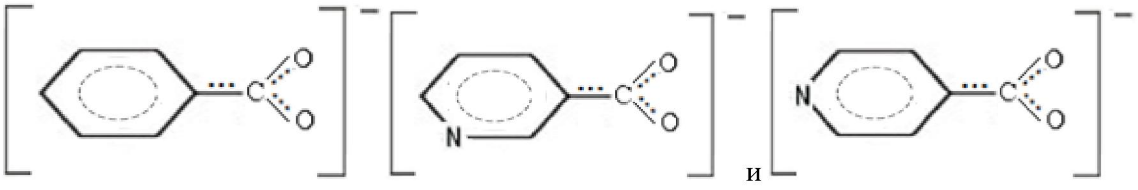
Comparing them in pairs, one can see that in spectra 4-6 there are no absorption bands characteristic of acids (a very strong band of the stretching vibration of the C = O group at 1700 cm^{-1}for benzoic and 1725 cm^{-1}for nicotinic and isonicotinic acids: about 1300 cm^{-1}- stretching vibration of C-O bonds, about 1400 cm^{-1}for nicotinic and isonicotinic acids and 940 cm^{-}

^{1}for benzoic acid, related to non-planar deformation vibrations of the OH group).The continuous absorptionhas been disappeared, characteristic for both acids and anion exchanger. The intensity of the band in the region of deformation vibrations of water (1600-1700 cm^{-1}) has sharply decreased. At the same time, a very intense pair of bands appeared at 1370 and 1620 cm^{-1}(1615 cm^{-1}for the reaction product of benzoic acid). This pair of bands should be attributed, respectively, to symmetric and antisymmetric stretching vibrations of the group - COO- adsorbed on the surface, according to [19,20]. In addition, absorption bands at 1560 cm^{-1}for isonicotinic and 1575 cm^{-1}for nicotinic and benzoic acids appeared in spectra 4-6.

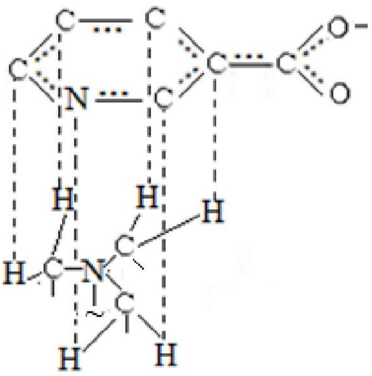
In [21] the origin of the band in the region 1550-1600 cm^{-1}is explained by the oscillation of the skeleton of the ring, and the increase in its intensity by conjugation. As for conjugation, we can agree with the statement, since the conjugation between the group  and the benzene and pyridine rings should be strong.

The observed changes in the spectra of the products of the interaction of acids with anion exchanger suggest a rearrangement of the structure of the molecules: the proton of the acid breaks off, neutralizing the groupings $H_{2n-1}O_n^-$ to water.

Formedanions



become counter ions of positively charged fixed centers of the resin surface. The absence of continuous absorption in the spectra of the interaction products indicates that there are no bridged hydrogen bonds between the water molecules and the oxygen atoms of the carboxylate groups with proton transfer, ie, in contrast to the formate anion, aromatic carboxylate anions of non-carboxylate-hydrate rings.This implies that the negative charge on the oxygen atoms of the carboxylate groups is insufficient to form such bonds.The results confirm the presence of conjugation between the aromatic rings and the carboxylate group in the anions and the large double bond of the C-C bond between these groups, which is probably responsible for the appearance of an intense band in the field of 1560-1600 cm^{-1}. Along with this, it is pointed out in [19] that the plane of the aromatic nucleus of adsorbed molecules is located parallel to the surface of the adsorbent.



Therefore, it can be assumed that most of the negative charge in these ions is at the center of the aromatic or heterocyclic nucleus. These rings seem to surround the fixed cation of anionite like carboxylate hydrate rings, stabilizing due to interactions between π-electrons of the ring and quaternary ammonium of hydrogen atoms.

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ИОНИТТЕРДІҢ ОРГАНИКАЛЫҚ СУБСТРАТТАРМЕН СУПРАМОЛЕКУЛЯРЛЫ КОМПЛЕКСТЕРІ

Аннотация. Қарастырылып отырған жұмыста ИҚ- спектроскопия әдісімен аромтты және гетероциклді қышқылдардың АВ-17-8 анионитімен әрекеттесуінің жалпы заңдылықтары зерттелген. Адсорбцияны статикалық жағдайда жүргізеді. Әрекеттесудің сипаты жөнінде алдымен дайындалған және өңдеуден өткен ионит үлгілерінің спектрограммаларында жаңа жолақтардың пайда болуына, олардың максимумдарының ығысуына және интенсивтіліктің өзгерістеріне қарай талдайды. Анионитттің ОН –формасының және оны органикалық қышқылдармен араластырудан кейінгі ИҚ- спектрлері алынды. Анионит АВ-17-8 бетінде карбон қышқылдарының адсорбциясынан кейін алынған ИҚ-спектрлердің негізінде адсорбцияланған молекулалардың ионалмастырғыш шайырдың активті орталықтарымен түзілген әртүрлі агрегатты супрамолекулярлы комплекстері ұсынылған. Молекулаішілік резонанстың жоғары дәрежесі мен анионитте адсорбция кезінде аниондардың түзілуіне байланысты ең жақсы адсорбциялану бейімділігі пиридинді орынбасушылары бар молекулаларға тән екендігі көрсетілген. Қышқылдардың адсорбциясы адсорбент бетінде орналасқан гидроксил топтарымен сутектік байланыстар түзу есебінен жүзеге асатындығы анықталған. Органикалық қышқылдардың адсорбциясынан кейін аниониттің спектрлерінде симметриялы және антисимметриялы валенттік тербелістерге сәйкес карбоксилат аниондардың сіңіру жолақтары табылған.

Түйін сөздер: адсорбция, карбон қышқылдары, анионит.

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СУПРАМОЛЕКУЛЯРНЫЕ КОМПЛЕКСЫ ИОНИТОВ С ОРГАНИЧЕСКИМИ СУБСТРАТАМИ

Аннотация. В настоящей работе методом ИК- спектроскопии изучены общие закономерности взаимодействия ароматических и гетероциклических кислот с анионитом АВ-17-8. Адсорбцию изучали в статических условиях. О характере взаимодействия судили по появлению новых полос, сдвигу их максимумов и изменению интенсивности на спектрограммах свежего и отработанных образцов ионита. Были получены ИК-спектры поглощения свежеприготовленного анионита в ОН- форме и после перемешивания его с органическими кислотами. На основании данных по ИК-спектрам анионита АВ-17-8 после адсорбции карбоновых кислот предложены различные агрегатные супрамолекулярные комплексы адсорбированных молекул с активными центрами ионообменной смолы. Показано, что наилучшую склонность адсорбироваться имеют молекулы с пиридинпроизводными заместителями, благодаря высокой степени внутримолекулярного резонанса и образованию анионов при адсорбции на анионите. Установлено, что адсорбция кислот осуществляется за счет образования водородной связи с гидроксильными группами, расположенными на поверхности адсорбента. В спектрах анионита после адсорбции органических кислот обнаружены полосы поглощения, соответствующие симметричным и антисимметричным валентным колебаниям карбоксилат анионов.

Ключевые слова: адсорбция, карбоновые кислоты, анионит.