Environment Protection Engineering

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SORPTION PROPERTIES OF POLYMERIC ADSORBENTS WITH RESPECT TO ISOMERIC AROMATIC COMPOUNDS

The results of sorption of nitrophenol and nitroaniline isomers are presented. The experiments were carried out by static and dynamic methods with porous copolymers styrene/divinylbenzene (S/DVB) and acrylonitrile/divinylbenzene (AN/DVB) having similar morphological characteristics. It has been found that there are no significant differences in the sorption behaviour of the two copolymers, despite the difference in polarities of their surfaces. For both the sorbents the nitrophenol isomers are adsorbed in the following order: ortho > para > metha. The sorption of nitroaniline isomers on the S/DVB sorbent proceeds as follows: ortho > para > metha, while on the AN/DVB sorbent its order changed being: ortho > metha > para.

1. INTRODUCTION

Sorption in aqueous solutions depends on interactions of sorbate and solvent molecules with the sorbent surface and molecules of any other component present in the solution. Thus, the specific surface area of sorbent and its polarity should significantly influence the degree of sorption. Both properties can easily be changed by varying the conditions of the synthesis of polymeric adsorbents and by using specific monomers.

In our earlier work the series of copolymers which differed in porosity and pore size distribution have been obtained by varying the synthesis conditions of styrene/divinylbenzene (S/DVB) copolymers. Sorption abilities of these copolymers with respect to aqueous solutions of phenol and its derivatives were determined in order to select the one having the best sorption properties [10]. In this copolymer the substitution of acrylonitrile for styrene under the same synthesis conditions gave a strongly polar adsorbent with nitrile groups (AN/DVB). It was expected that this adsorbent should exhibit an increased sorption with respect to compounds having high dipole moment values, i.e. molecules of the B group according to the classification by KISELEV [5–7]. Copolymers of this kinds should also exhibit strong specific interactions with sorbate molecules forming hydrogen bonds, i.e. molecules of the D group.

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Previous studies on phenol, p-nitrophenol, and p-nitroaniline sorption from their aqueous solutions on S/DVB and AN/DVB copolymers have shown that the polarity of sorbent surface has no marked effect on this process [11]. The sorption degree of the separated compounds differed very little from one other, being dependent on dipole moments and solubilities of the sorbate molecules. Due to the specific intermolecular interaction among the solution components their interaction with the adsorbent surface decreases; thus, with the increasing solubility of the sorbate its sorption on the sorbent surface decreases [4].

In this work the results of studies of the effect of substituent position in nitrophenol and nitroaniline on their sorption on porous S/DVB and AN/DVB copolymers are presented.

2. EXPERIMENTAL

The porous copolymers of styrene and divinylbenzene (S/DVB) and acrylonitrile and divinylbenzene (AN/DVB) were prepared using the standard suspension technique. The selected properties of the copolymers are listed in tab. 1. The morphological and physical characteristics of the copolymers were obtained according to the methods described earlier [8]. The sorption properties measured under static and dynamic conditions were also presented [11].

Table 1

Morphological and physical characteristics of the copolymers studied

Morfologiczna i fizyczna charakterystyka badanych kopolimerów

Parameter	S/DVB	AN/DVB
Skeletal density, g/cm^3	1.07	1.14
Apparent density, g/cm^3	0.574	0.599
Specific volume, cm^3/g	0.81	0.79
Specific surface area, m^2/g	492	465
Pore radius distribution, %:		
10–100 nm	87.6	88.0
100–1000 nm	9.3	10.4
1000–7500 nm	3.1	1.6
Mechanical strength, kG/cm^2:		
dry	322	434
in water	52	415
in toluene	47	145

3. RESULTS AND DISCUSSION

In tab. 1 the morphological characteristics of S/DVB and AN/DVB copolymers are presented. The data indicate that both copolymers have similar porous properties. However, the substitution of acrylonitrile for styrene gave copolymers of considerably higher mechanical strength, which is an important factor when these products are used in dynamic sorption processes. Table 2 reports some physicochemical properties of the adsorbates having a possible effect on mechanism of sorption and its degree.

Table 2

Some properties of the sorbates
Niektóre właściwości sorbatów

Sorbate	Solubility in water g/100 cm^3	Dipole moment D
o-nitrophenol	0.32^{38}	3.10
m-nitrophenol	1.35^{25}	3.90
p-nitrophenol	1.52^{25}	5.05
o-nitroaniline	0.121^{25}	4.25
m-nitroaniline	0.09^{25}	4.94
p-nitroaniline	0.057^{25}	6.32

The sorption isotherms of different nitroaniline isomers on the copolymers studied are shown in figs. 1 and 2. They indicate that the process is independent of the sorbent structure and that it proceeds according to a common mechanism. In both cases these Langmuir-type isotherms are characterized by an initially acute increase of the sorption with the increasing concentration of the external solution, followed by a gradually approach to a limiting value corresponding to the adsorption of a monomolecular layer. This value cannot be attained, however, since the water solubility of the studied compounds is too low (tab. 2). Similar sorption isotherms were observed for nitrophenol isomers. According to GILES et al. [2, 3], the shape of sorption isotherms depends on sorption mechanism, orientation of the adsorbed molecules, and possible changes of this orientation. The isotherms shown in figs. 1 and 2, according to the GILES classification, belong to the L class which includes compounds the molecules of which can take a parallel position toward the adsorbent surface. Obviously, the orientation of the adsorbed molecules depends on the nature of interactions either between molecules and surface, or among the components in the solution. The position of adsorbed molecules can also be changed by changing the concentration of the equilibrium solution [1]. However, parameters affecting a given orientation are very complicated and difficult to determine. As to the isomers of nitrophenol and nitroaniline no definite conclusion regarding their orientation on the surface of the studied sorbents could be formulated becasue of the very low water solubility of these compounds. Therefore the limiting sorption has not been attained.

The distribution coefficient K_D, which is a measure of the retention of a given compound on the sorbent surface, has the following from:

$$K_D = \frac{\text{weight of a compound adsorbed by 1 g of sorbent}}{\text{weight of compound in 1 cm}^3 \text{ of solution}}.$$
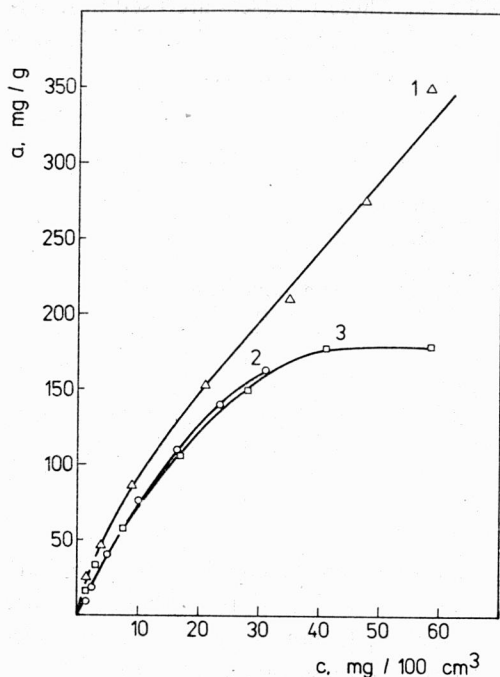

Fig. 1. Isotherms of nitroaniline isomers sorption
on S/DBV copolymer surface
1 — ortho, 2 — para, 3 — metha

Rys. 1. Izotermy sorpcji izomerów nitroaniliny
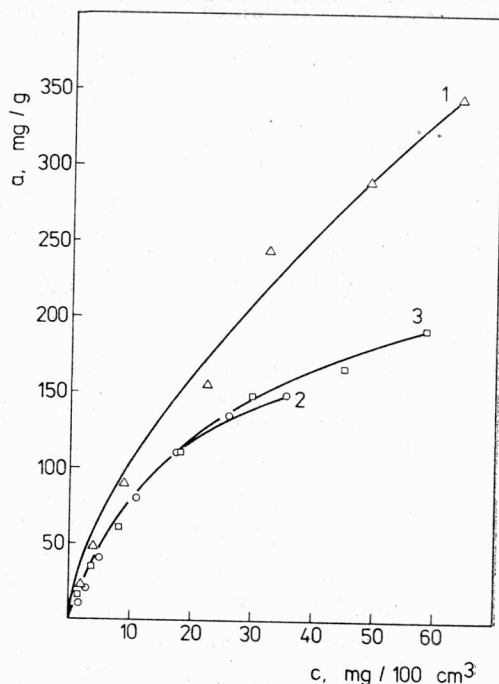na powierzchni kopolimeru S/DVB
1 — orto, 2 — para, 3 — meta

Fig. 2. Isotherms of nitroaniline isomers sorption
on AN/DVB copolymer surface
1 — ortho, 2 — para, 3 — metha

Rys. 2. Izotermy sorpcji izomerów nitroaniliny
na powierzchni kopolimeru AN/DVB
1 — orto, 2 — para, 3 — meta

The values of K_K for nitrophenol and nitroaniline on S/DVB and AN/DVB surfaces are block-diagrammed in fig. 3. These data indicate that the sorption properties of both the studied copolymers with respect to aqueous solutions of nitrophenol and nitroaniline isomers are very small.

The results of the sorption performed by the dynamic method are shown in figs. 4 and 5, and summarized in tab. 3. They confirm the previous observation that the polarity of AN/DVB copolymer surface has no significant effect on the sorption of nitrophenol and nitroaniline. The isomers of nitrophenol are adsorbed on both the surfaces in the following order: ortho > para > metha. This relationship is in agreement with their decrea-

sing solubility, but it is inversely proportional to their increasing dipole moments (tab. 2). The sorption of nitroaniline isomers on the S/DVB sorbent surface increases as follows: ortho > para > metha, and on the AN/DVB sorbent surface as follows: ortho > metha > para. These sequences cannot be directly related to any of the mentioned properties of
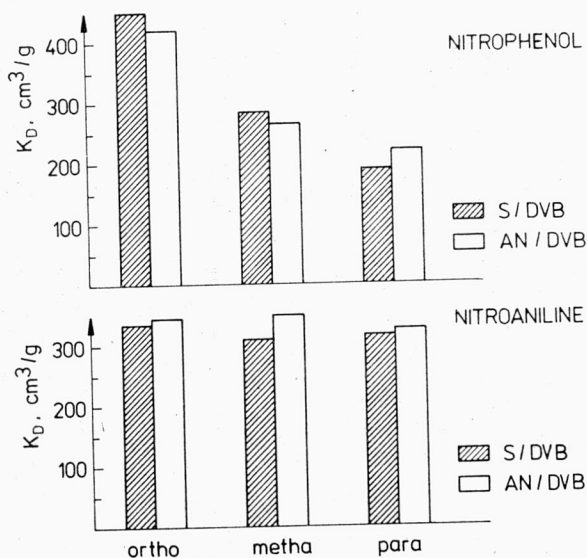

Fig. 3. Distribution coefficient for nitrophenol and nitroaniline isomers on S/DVB and AN/DVB copolymers

Rys. 3. Współczynnik podziału dla izomerów nitrofenolu i nitroaniliny na kopolimerach S/DVB i AN/DVB
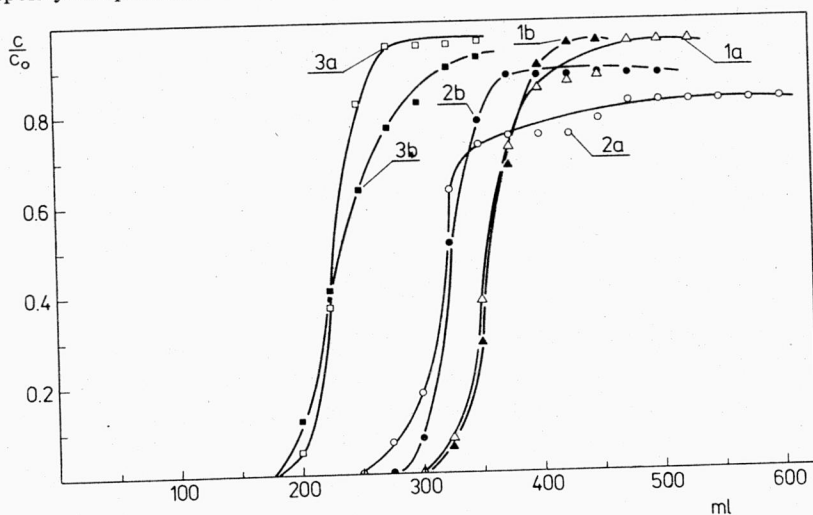

Fig. 4. Sorption of nitroaniline isomers on S/DVB copolymer measured by the dynamic method
1 — ortho, 2 — para, 3 — metha, a — 1st cycle, b — 2nd cycle

Rys. 4. Sorpcja izomerów nitroaniliny na kopolimerze S/DVB zmierzona za pomocą metody dynamicznej
1 — orto, 2 — para, 3 — meta, a — pierwszy cykl, b — drugi cykl

Table 3

Sorption results by the dynamic method

Wyniki sorpcji zmierzonej metodą dynamiczną

Sorbate	S/DVB		AN/DVB	
	1st cycle	2nd cycle	1st cycle	2nd cycle
o-nitrophenol				
Breakthrough capacity, mg/g	204.2	186.4	191.8	172.7
Total capacity, mg/g	238.5	229.8	252.5	251.6
Desorption yield, %	86	88	100	92.5
m-nitrophenol				
Breakthrough capacity	127.8	127.9	184.2	184.2
Total capacity	144.0	145.6	267.5	270
Desorption yield	100	100	—	—
p-nitrophenol				
Breakthrough capacity	106.5	127.8	153.5	161.1
Total capacity	141.6	159.4	198.7	207.6
Desorption yield	92.3	87.3	89.2	85
o-nitroaniline				
Breakthrough capacity	234.4	255.7	276.2	414.4
Total capacity	306.1	302.1	455.3	510.5
Desorption yield	83.8	100	100	100
m-nitroaniline				
Breakthrough capacity	149.2	149.2	253.2	253.2
Total capacity	192.1	201.1	324.7	289.9
Desorption yield	88.7	100	99.2	100
p-nitroaniline				
Breakthrough capacity	213.0	234.4	184.1	184.1
Total capacity	306.5	282.5	306.6	339.8
Desorption yield	84	100	90.7	90.3

the nitroaniline isomers. In conclusion, the systems composed of a polar or non-polar sorbent, a polar solvent, and a polar sorbate behave in a complicate way. The reciprocal interactions being not known, the structure of a sorbent cannot be correlated to its sorption properties. This is particularly true in case of dipole moment, which is usually determined in the gas phase or in a non-polar solvent. The best sorption properties exhibited by both the ortho isomers can be explained by the formation of intermolecular hydrogen bonds which enhance the affinity of these isomers towards the sorbents, all the more so as a decrease in the water–sorbate interaction, compared with the other isomers, can be postulated.
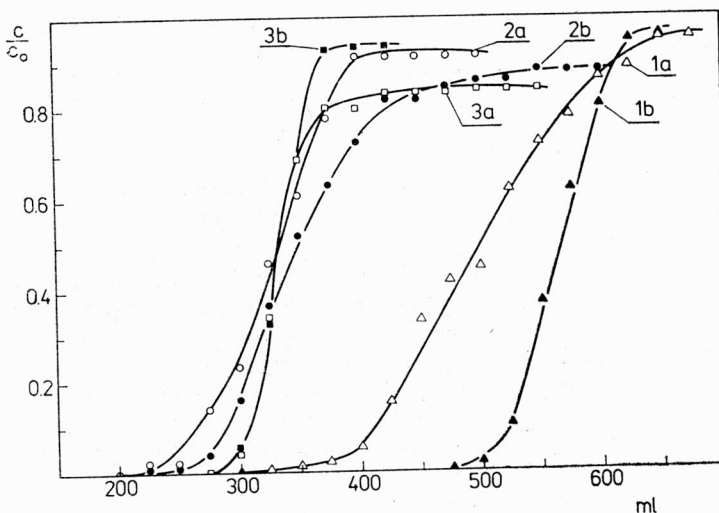
Fig. 5. Sorption of nitroaniline isomers on AN/DVB copolymer measured by the dynamic method
For explanations see fig. 4

Rys. 5. Sorpcja izomerów nitroaniliny na kopolimerze AN/DVB zmierzona za pomocą metody dynamicznej
Objaśnienia jak na rys. 4.

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WŁAŚCIWOŚCI SORPCYJNE ADSORBENTÓW POLIMERYCZNYCH W STOSUNKU DO NIEKTÓRYCH IZOMERÓW ZWIĄZKÓW AROMATYCZNYCH

Przedstawiono wyniki sorpcji izomerów nitrofenolu i nitroaniliny. Doświadczenia z porowatymi kopolimerami styren/dwuwinylobenzen (S/DVB) i akrylonitryl/dwuwinylobenzen (AN/DVB) o podobnych charakterystykach morfologicznych prowadzono metodą statyczną i dynamiczną. Nie stwierdzono istot-

nych różnic w sorpcji obu kopolimerów pomimo różnic w polarności ich powierzchni. W obu sorbentach izomery nitrofenolu są adsorbowane w następującym porządku: orto > para > meta. Sorpcja izomerów nitroaniliny na S/DVB przebiega następująco: orto > para > meta, a na AN/DVB — orto > meta > > para.

SORPTIONSEIGENSCHAFTEN VON POLYMEREN ADSORPTIONSMITTELN GEGENÜBER EINIGEN ISOMEREN VON AROMATEN

Erörtert wird die Sorption der Isomeren von Nitrophenol und -anilin. Untersuchungen mit porösen Kopolymeren Styren/Divinylbenzol (S/DVB) und Akrylnitryl/Divinylbenzol (AN/DVB) von ähnlicher morphologischer Charakteristik, wurden nach der statischen und dynamischen Verfahrensweise durchgeführt. Die Resultate der Sorption beider Kopolymere unterscheiden sich kaum voneinander obwohl der Differenzen in der Polarität ihrer Oberflächen. Die Isomere des Nitrophenols werden auf beiden Sorptionsmitteln in der Reihenfolge: orto > para > meta adsorbiert. Die Sorption der Isomere der Nitroanilin verläuft auf S/DVB in der Reihenfolge: orto > para > meta, auf AN/DVB dagegen in der Reihenfolge: orto > meta > para.

СОРБЦИОННЫЕ СВОЙСТВА ПОЛИМЕРНЫХ АДСОРБЕНТОВ ПО ОТНОШЕНИЮ К НЕКОТОРЫМ ИЗОМЕРАМ АРОМАТИЧЕСКИХ СОЕДИНЕНИЙ

Представлены результаты сорбции изомеров нитрофенола и нитроанилина. Опыты по пористым сополимерам стирол/дивинилбензол (С/ДВБ) и акрилонитрил/дивинилбензол (АН/ДВБ) со сходными морфологическими характеристиками проводились статическим и динамическим методами. Не было выявлено существенных различий в сорбции обоих сополимеров, несмотря на различия в полярности их поверхностей. В случае обоих сорбентов изомеры нитрофенола адсорбируются в следующем порядке: орто > пара > мета. Сорбция изомеров нитроанилина на С/ДВБ проходит следующим образом: орто > пара > мета, а на АН/ДВБ — орто > мета > пара.