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Adsorption of Pyridine from Various Solvents by Specific Adsorbents

Adsorpcja pirydyny z różnych rozpuszczalników na specyficznych adsorbentach

Адсорбция пиридина из различных растворителей на специфических адсорбентах

In view of the growing interest in the phenomenon of specific adsorption, a number of investigations in this field have been carried out in this department [1—5]. Specific adsorption of pyridine from decaline solutions has been shown for silica gels activated with some heterocyclic bases.

The separation of mixtures and purification of substances by selective adsorption depends primarily upon the choice of a suitable solvent. The lower polarity of the adsorbed substance, the stronger is its adsorption from a polar solvent by non-polar adsorbent, and *vice versa*, a polar substance is more strongly adsorbed by a polar adsorbent from a non-polar solvent [6]. The chemical nature of the adsorptive and of the solvent also plays an important role.

Therefore, it seemed interesting to investigate to what degree the kind of a solvent influences the specificity of adsorption.

In order to answer this question, the adsorption of pyridine from various solvents by pyridine activated silica-gel has been measured; parallel measurements have been carried out for the reference gel.

EXPERIMENTAL

The silica gels were prepared by the method reported in an earlier paper [1]. The gels were marked as in the earlier paper [1]:

reference gel DS5

gel activated with pyridine D2P5

The following solvents were investigated: benzene, carbon tetrachloride, cyclohexane, cyclohexene, cyclohexanon, tetralin, water, acetone, toluene, and n-butyl alcohol.

All organic solvents were dehydrated by means of dry silica-gel. Adsorption was investigated by the static method, measuring the concentrations by means of a Zeiss-Jena refractometer.

The adsorption was calculated from the formula

$$x^{(v)} = \frac{(c_0 - c)\,v}{m}$$

where

c_0 — initial concentration of the solution

c — concentration of the solution after adsorption

v — volume of the adsorbent

The results are given in Figs. 1, 2, 3 in the form of adsorption isotherms.

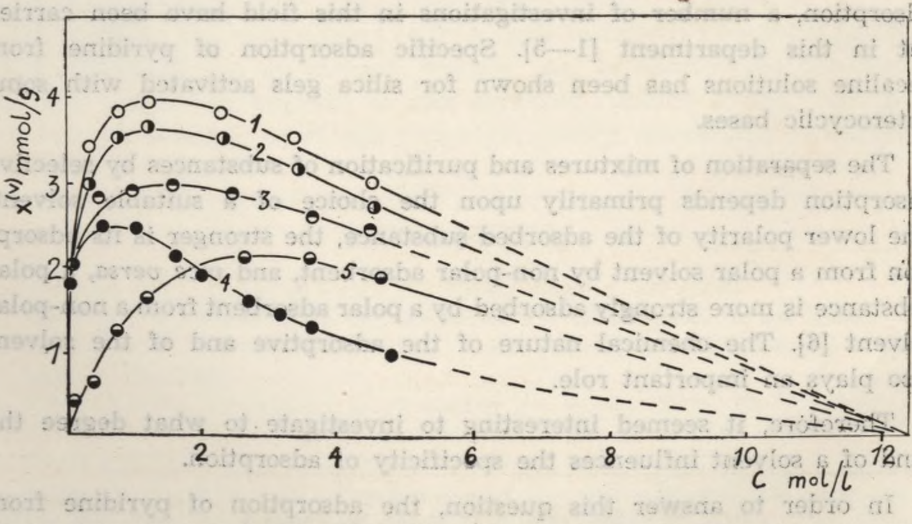

Fig. 1. Adsorption isotherms of pyridine from: 1 — carbon tetrachloride, 2 — cyclochexane, 3 — toluene, 4 — benzene, 5 — cyclohexanon solutions on D2P5-gel

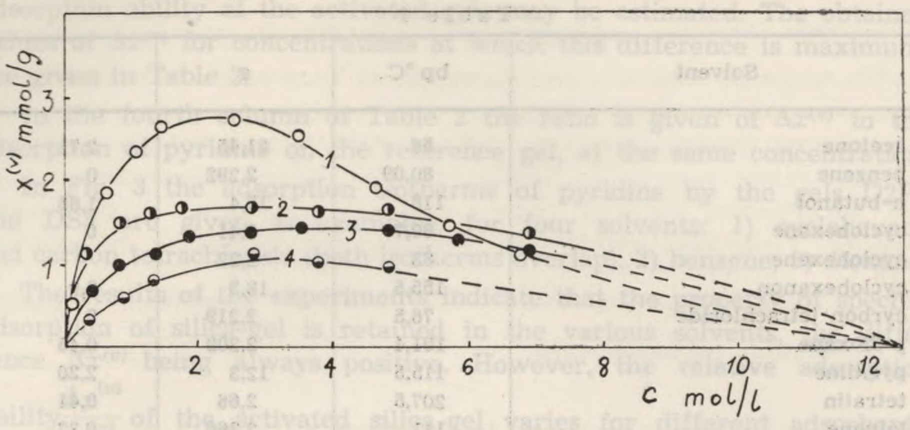

Fig. 2. Adsorption isotherms of pyridine from: 1 — water, 2 — n-butanol, 3 — acetone, 4 — dioxane solutions on D2P5-gel

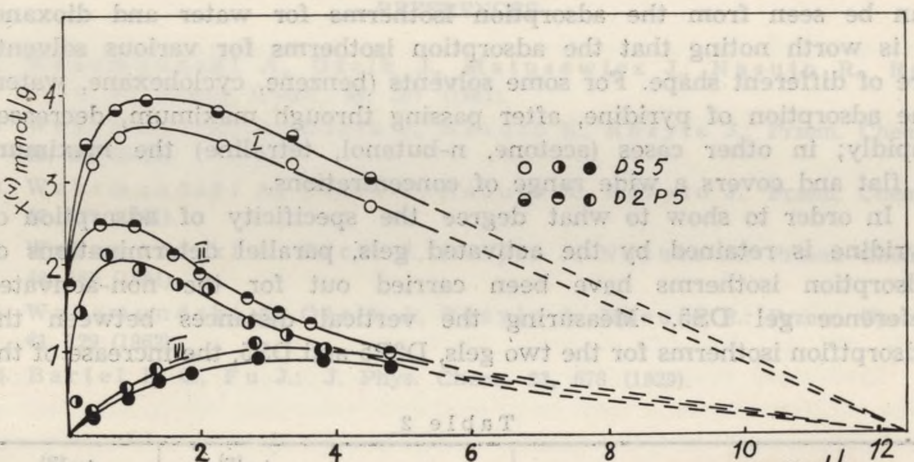

Fig. 3. Adsorption isotherms of pyridine from: I — carbon tetrachloride, II — benzene, III — dioxane solutions on DS5 and D2P5-gels

DISCUSSION

As can be seen from the diagrams, the shape of adsorption isotherms of pyridine for the specific silica-gel depends upon the kind of solvent from which pyridine is adsorbed. The main factor determining the magnitude of adsorption is the dielectric constant and the dipole moment of the solvent (Table 1).

Table 1

Solvent	bp °C	ε	μ
acetone	56	21,45	2,71
benzene	80,09	2,292	0
n-butanol	118	17,4	1,65
cyclohexane	80,7	2,41	0
cyclohexene	83	2,22	0
cyclohexanon	155,5	18,3	2,9
cyrbon tetrachloride	76,5	2,219	0
p-dioxane	101,4	2,209	0,45
pyridine	115,5	12,3	2,20
tetralin	207,5	2,66	0,41
toluene	111	2,366	0,37
water	100	88	1,84

However, it cannot be stated that this correlation is complete, as can be seen from the adsorption isotherms for water and dioxane. It is worth noting that the adsorption isotherms for various solvents are of different shape. For some solvents (benzene, cyclohexane, water) the adsorption of pyridine, after passing through maximum, decreases rapidly; in other cases (acetone, n-butanol, tetraline) the maximum is flat and covers a wide range of concentrations.

In order to show to what degree the specificity of adsorption of pyridine is retained by the activated gels, parallel determinations of adsorption isotherms have been carried out for the non-activated reference gel DS5. Measuring the vertical distances between the adsorptfion isotherms for the two gels, D2P5 and DS5, the increase of the

Table 2

Solvent	c mol/1	$\Delta x^{(v)}$ mmol/g	$\frac{\Delta x^{(v)}}{x^{(v)}}$
acetone	3,65	0,16	0,129
benzene	0,075	1,0	0,91
n-butanol	2,75	0,16	0,102
cyclohexane	2,8	0,4	0,121
cyclohexene	1,35	0,20	0,157
cyclohexanon	2,8	0,20	0,1
carbon tetrachloride	3,68	0,4	0,109
p-dioxane	3,0	0,16	0,182
tetralin	3,35	0,28	0,115
toluene	0,15	0,8	0,421
water	2,15	0,32	0,133

adsorption ability of the activated gels may be estimated. The obtained values of $\Delta x^{(v)}$ for concentrations at which this difference is maximum, are given in Table 2.

In the fourth column of Table 2 the ratio is given of $\Delta x^{(v)}$ to the adsorption of pyridine on the reference gel, at the same concentration.

In Fig. 3 the adsorption isotherms of pyridine by the gels D2P5 and DS5 are given as examples, for four solvents: 1) cyclohexane and carbon tetrachloride (both isotherms overlap), 2) benzene, 3) dioxane.

The results of the experiments indicate that the property of specific adsorption of silica-gel is retained in the various solvents, the difference $\Delta x^{(v)}$ being always positive. However, the relative adsorption ability $\frac{\Delta x^{(v)}}{x^{(v)}}$ of the activated silica-gel varies for different adsorbents, decreasing with diminishing adsorption.

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STRESZCZENIE

Zbadano wpływ rodzaju rozpuszczalnika na wielkość adsorpcji pirydyny na żelu krzemionkowym uaktywnianym na tę substancję oraz na żelu porównawczym. Stwierdzono, że adsorpcja pirydyny zależy od charakteru chemicznego rozpuszczalnika i jego własności fizycznych (stała dielektryczna i moment dipolowy). Wykazano, że względna zdolność adsorpcyjna $\frac{\Delta x^{(v)}}{x^{(v)}}$ zmniejsza się wraz ze zmniejszeniem się wielkości adsorpcji pirydyny z poszczególnych rozpuszczalników.

РЕЗЮМЕ

Исследовано влияние растворителя на величину адсорбции пиридина на геле кремневой кислоты активированным этим веществом, а также на стандартном геле. Обнаружено, что адсорбция пиридина на этих гелях зависит от химического характера растворителя и от его физических свойств (делектрическая константа и дипольный момент). Отмечено, что его релятивная адсорбционная способность $\frac{\Delta x^{(v)}}{x^{(v)}}$ уменьшается с уменьшением величины адсорбции пиридина из различных растворителей.

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