SORPTION EQUILIBRIA OF PYRIDINE DERIVATIVES IN AQUEOUS SOLUTION ON POROUS RESINS AND ION EXCHANGE RESINS

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Studies have been made of the sorption equilibria of pyridine, picoline and lutidine in aqueous solution on ion-exchange and porous resins. The sorption behaviors of these pyridines on strong acid ion-exchange resin can be expressed by the Langmuir isotherms, and those on both weak acid ion-exchange and porous resins by the Freundlich isotherms. The sorption mechanisms followed either a neutralization reaction with the H-form ion-exchange resins, or a hydrophobic interaction with the porous resins. Methanol content of the aqueous solution as well as solution pH was found to have a significant effect on the sorption of pyridines.

Furthermore, the separations of these pyridines from each other were examined for three binary solute solutions in a batch mode. The pyridines were sorbed preferentially on the resins in the following sequence:

pyridine < 3-picoline < 3, 5-lutidine

where the selectivity increased as follows:

strong acid ion-exchange resin < weak acid ion-exchange resin < porous resin.

Introduction

Pyridines are heterocyclic, aromatic amines, in which one of the CH-groups in benzene is replaced with nitrogen. They are in general harmful to living things. These amines are frequently present in effluents from plants of several industries such as rubber and plastics, petrochemicals and some other organochemical industries[8]. Thus the removal and recovery of pyridines from wastewater are important problems, due both to the difficulty in treating them by the usual activated sludge method and to the necessity of reusing relatively expensive chemicals.

Sorption methods offer an effective removal and separation of organic, weak base species from aqueous media, and have been studied extensively on several sorbents, *e. g.*, activated carbon[5, 6], porous resins[1, 3, 6, 9] and ion-exchange resins[4, 10, 11]. For example, Pahari and Sharma[6] studied the column separation of pyridines with XAD-4, and Stuber and Leenheer[7] did so with XAD-8. Gilmer and Pietrzyk[2] investigated sorption characteristics of several organic bases including pyridines on a cation exchange resin. However, it is still important to conduct a systematic study of these sorption equilibria of pyridines to explore a sorbent that provides selective separation.

This study was conducted to confirm the possibilities of separation of pyridines from aqueous media on such polymeric resins as Amberlite XAD, strong and weak acid ion-exchange resins. Pyridine and two of its derivatives were selected as model heterocyclic amines:

pyridine, 3-picoline (3-methylpyridine) and 3, 5-lutidine (3,5-dimethylpyridine). The sorption characteristics were studied in terms of sorption isotherms and separation factors in a batch operation.

1. Experimental

1.1 Materials

Four Amberlites, XAD-2, 4, 7 and 8 were used as porous resins with no functional group; the former two are styrene-divinylbenzene, the latter two being acrylic-ester copolymers. Both XAD-2 and 4 have more hydrophobic surfaces than XAD-7 and 8. Two macroreticular ion-exchange resins were also selected: strong acid type with sulfonic group (Amberlite 200C) and weak acid type with carboxyl group (Amberlite IRC-50). All the resins used were obtained from Organo *Co., Ltd.*, and their properties are given in **Table 1**.

Prior to sorption experiments, the resins were washed by a conventional method. After removing surface water from the washed resins in a centrifuge (3000 r.p.m.; 10 min.), the purified resins were stored in a bottle. Water content of the resins was determined from weight loss before and after drying at 378 K for 20 hr, and the results are also given in Table 1.

Aqueous solutions of pyridine, 3-picoline and 3, 5-lutidine were prepared by dissolving the respective solutes in deionized water with no adjustment of pH. All the chemicals used were of reagent grade.

1.2 Sorption equilibria

All the experiments were carried out batchwise.

Table 1. Properties of porous resins and ion-exchange resins used in this work

Resin	Material	Surface area (m^2/g)	Pore diameter (nm)	Exchange capacity (mol/kg)	Water content (%)
XAD-2	Styrene-DVB	280-320	9	—	41
XAD-4	Styrene-DVB	700-800	4	—	51
XAD-7	Acrylic-ester	350-500	9	—	67
XAD-8	Acrylic-ester	120-200	22.5	—	56
200C	Styrene-DVB	—	—	4.3	48 (H), 42 (Na)
IRC-50	Methacrylic-DVB	—	—	10.0	44 (H), 66 (Na)
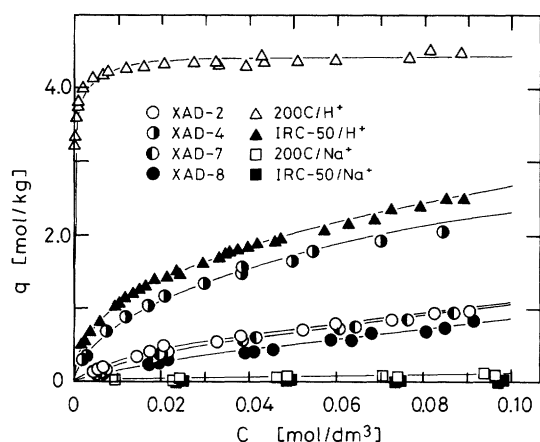
Fig. 1 Sorption isotherms of pyridine on porous resins and ion-exchange resins

Fig. 2 Sorption isotherms of 3-picoline on porous resins and ion-exchange resins. Keys are same as in Fig. 1.

2. Results and Discussion

2.1 Sorption isotherm

Figure 1 shows typical sorption isotherms of pyridine on the porous resins and ion-exchange resins. The concentration of solute in the resin phase was calculated as

$$q = (C_0 - C) V / W \qquad (1)$$

where C_0 and C denote the initial and equilibrium concentrations of the solute in the aqueous phase, V is the volume of the aqueous phase and W is the dry weight of the resin.

In the present experiments, little influence of the initial solute concentration in the aqueous phase on the
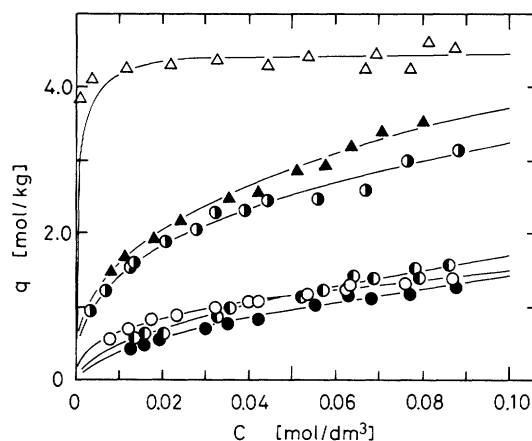
Sorption equilibrium was attained by shaking an appropriate amount of the resin and 20 cm^3 of an aqueous solute solution in a 50cm^3 glass-stoppered flask for 24 hr by use of a mechanical shaker maintained at 298 K. After equilibrating with the aqueous solution, the resin was separated from the solution, and the solute concentration in the solution was determined in a gas chromatograph with FID detector. Equilibrium solution pH was measured with a pH meter. Taking account of the water content of the resin, the resin's solute uptake at equilibrium was calculated from a mass balance on the basis of dry weight of the resin.

sorption equilibrium was found in the range measured; thus, each isotherm was obtained by changing either C_0 or W. The initial solute concentration ranged from 0.025 to 0.10 mol/dm^3, where the greater part of the pyridines might be present in free form owing to the weak base. As Fig. 1 shows, XAD-4 sorbed more pyridine than the other porous resins, because of its higher specific surface area. Although the uptake of pyridine was much smaller on XAD-2 than on XAD-4, the sorption amounts per unit surface area of the two resins are comparable. The uptakes on the acrylic-ester resins, XAD-7 and 8, were slightly smaller than on XAD-2.

Sorption of pyridine on both the strong acid 200C and weak acid IRC-50 ion-exchange resins was also examined. Pyridine was sorbed on the H-form 200C very strongly even in a low-concentration region, as can be seen in Fig. 1, whereas the extent of sorption on the Na-form 200C was less than 3%. This indicates that the sorption of pyridine on the strong acid ion-exchange resin follows not a physical sorption but a chemical one with a neutralization reaction between the weak base pyridine and the sulfonic group in the H-form 200C. The maximum q of the 200C was found to be 4.47 mol/kg, which is almost the same as the ion-exchange capacity.

In the case of the H-form IRC-50, the sorption amount of pyridine was much smaller than on the H-form 200C, and the Na-form IRC-50 also showed little sorption. Such a lowering of q might be due to a weak interaction between pyridine and the carboxyl group.

In **Figs. 2 and 3** the sorption isotherms of 3-picoline and 3, 5-lutidine respectively are shown. With increasing number of methyl groups in the pyridine ring, the hydrophobicity of these derivatives increases as follows:

pyridine < 3-picoline < 3, 5-lutidine
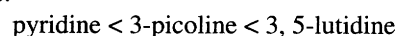
As would be expected, the concentration of the respective solutes in the four porous resins increased in the above sequence, owing to the hydrophobic interaction between the solutes and the resins. In particular, XAD-4 showed superior sorptibility, and the value of q for 3, 5-
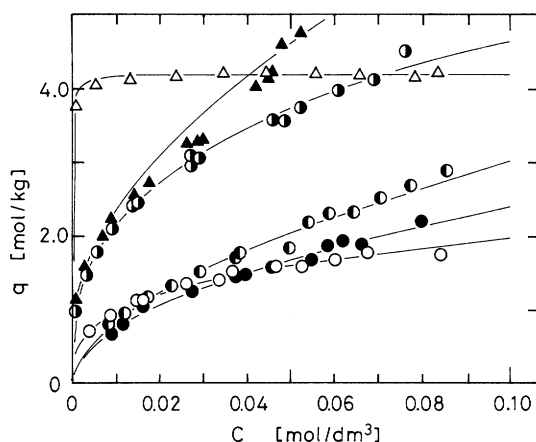
Fig. 3 Sorption isotherms of 3,5-lutidine on porous resins and ion-exchange resins. Keys are same as in Fig. 1.

Table 2. Sorption parameters of Langmuir formula,
$$q = Kq_0C / (1 + KC)$$

| | Adsorbate | | | | | |
| | pyridine | | 3-picoline | | 3, 5-lutidine | |
Resin	K	q_0	K	q_0	K	q_0
200C (H)	2095	4.47	1270	4.48	13441	4.20

lutidine exceeded that for the H-form 200C.

If sorption on the porous resins is caused only by the hydrophobic interaction, then an increase in sorptibility depends on the hydrophobicity of not only pyridine derivatives but also that of the resin. With increasing hydrophobicity of the solute, however, the values of q became greater for both XAD-7 and 8 than for XAD-4. This result implies that in addition to the hydrophobic interaction, hydrogen-bonding occurs between the nitrogen atom of the pyridine ring and the acryl-ester groups in the two resins.

The sorption isotherms of 3-picoline and 3, 5-lutidine on the H-form 200C were the same as that of pyridine; however, the values of q for the H-form IRC-50 increased in the sequence of the hydrophobicity. This corresponds with the order in the basicity of pyridines: the value of pKa is 5.22 for pyridine, 5.63 for 3-picoline and 6.15 for 3, 5-lutidine[12]. The interaction of pyridines with carboxyl groups of IRC-50 is thought to be stronger for more basic pyridines. Since ion-exchange capacities of weak acid ion-exchange resins are, in general, higher than those of strong acid resins, it might be effective to use a weak acid resin for relatively strong basic solutes.

As Figs. 1-3 show, the sorption isotherms of pyridine derivatives on the H-form 200C could be expressed with the Langmuir isotherms, and those on the other resins with the Freundlich isotherms. In **Tables 2 and 3**, the sorption parameters of the Langmuir and Freundlich formulas respectively are given. The solid lines in Figs. 1-3 represent the calculated values, and agree well with the experimental results.

2.2 Effects of solution pH and MeOH content

Figure 4 shows the effect of solution pH on the

Table 3. Sorption parameters of Freundlich formula,
$$q = kC^{1/n}$$

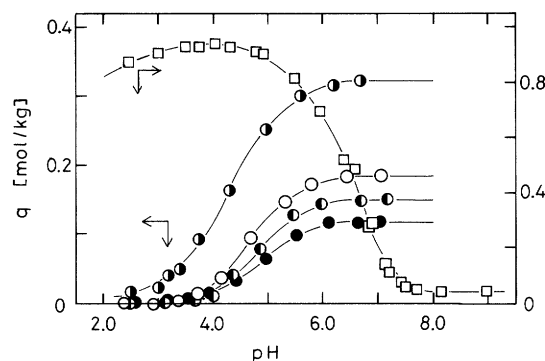| | Adsorbate | | | | | |
| | pyridine | | 3-picoline | | 3, 5-lutidine | |
Resin	k	n	k	n	k	n
XAD-2	4.37	1.67	3.41	2.79	4.02	3.23
XAD-4	7.48	2.03	7.36	2.80	10.27	2.94
XAD-7	5.18	1.47	6.24	1.77	10.74	1.80
XAD-8	4.65	1.38	5.39	1.74	7.57	1.99
IRC-50 (H)	6.93	2.43	8.83	2.68	16.00	2.41

Fig. 4 Effect of solution pH on the sorption of pyridine on porous resins and ion-exchange resin. Keys are same as in Fig. 1. $C_0 = 0.01$ mol/dm³, $W = 0.50 \times 10^{-3}$ kg for porous resins, $W = 0.175 \times 10^{-3}$ kg for ion-exchange resin.

sorption of pyridine on the porous resins, where the pH was adjusted by adding a small amount of NaOH or HCl. Since pyridines are weak base, the sorption characteristics are affected by the solution pH: the highest sorption is observed at high basicities in the presence of free pyridine, and the lowest sorption at high acidities in the presence of its protonated pyridine. With increasing pH the uptake of pyridine on the resin attained a plateau above the pKa of pyridine, 5.22. All the sorption results for the four porous resins showed a similar pH dependency, though being different in q from one another, as described in the previous section.

In contrast, sorption on the Na-form 200C occurred at high acidities as a result of an ion-exchange reaction between the Na⁺ ion in 200C and the protonated pyridine, as shown in Fig. 4. In the more acidic region, however, the extent of sorption tends to decrease because of the participation of H⁺ ion in the exchange reaction. Such sorption behaviors are useful in selecting the resin for treating an aqueous medium at a given pH; moreover, it is a great advantage that the resin can easily be regenerated with either acid or base solution. However, for 3, 5-lutidine a significant amount was sorbed even in its protonated form, though the data are not given. This implies that high regeneration is impossible with acid solutions as a regenerant.

Here, we attempted the possibility of regeneration with methanol solution. The effect of MeOH content in the aqueous solution on the sorption of pyridine is shown in **Fig. 5**. With increasing MeOH content a
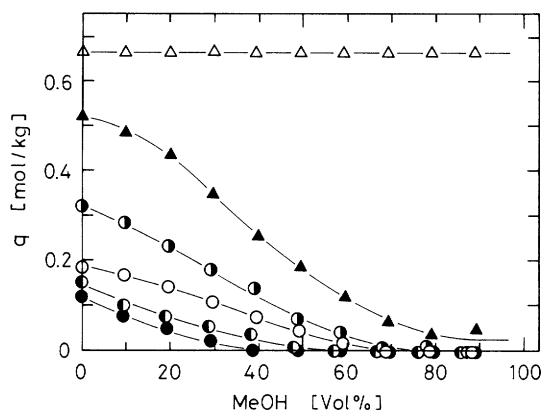
Fig. 5 Effect of methanol content on the sorption of pyridine on porous resins and ion-exchange resins. Keys are same as in Fig. 1. $C_0 = 0.01$ mol/dm³, $W = 0.50$ x 10^{-3} kg for porous resins, $W = 0.175$ x 10^{-3} kg for ion-exchange resins.

decrease in q was observed not only for the porous resins but also for the H-form IRC-50, owing to enhancement of the affinity for pyridine to the solution. This suggests that the regeneration of the porous resins-sorbed pyridine is attainable by using MeOH as a regenerant. In the case of strong acid ion-exchange resin, however, the sorption of pyridine was not affected by the addition of MeOH.

2.3 Separation of pyridine derivatives

The application of porous resins or ion-exchange resins to the separation of pyridines was examined in a batch operation. **Figure 6** shows the equilibrium relations between the fractional concentrations of pyridines in both phases for sorption on XAD-4 as a plot of $\overline{[B]}/(\overline{[A]}+\overline{[B]})$ against $[B]/([A]+[B])$, where A and B denote the respective solutes, and the overbar denotes the resin phase. The experimental conditions are given in **Table 4**. As Fig. 6 shows, the equilibrium data located on the convex curves, indicating a selective sorption of solute B over A on XAD-4. The selective sorption is in the following sequence:

pyridine < 3-picoline < 3, 5-lutidine.

We defined the separation factor α as

$$\alpha = (\overline{[B]}/[B])/(\overline{[A]}/[A]) \tag{2}$$

The values of α, determined by the least squares method, are given in Table 4. In Fig. 6 the solid lines are calculated from these values.

The separation of pyridines on the porous resins can be attributed mainly to the difference in hydrophobic interaction between the solute and the polymeric matrix. 3-picoline and 3, 5-lutidine have one more methyl group than pyridine and 3-picoline, respectively; thus, there is close agreement between the separation factors of pyridine/3-picoline and 3-picoline/3, 5-lutidine, as would be expected. For 3, 5-lutidine, having two methyl groups, the separation factor gives a much higher value, 32.95, and an appropriate separation of pyridine from its homologous series could be expected.
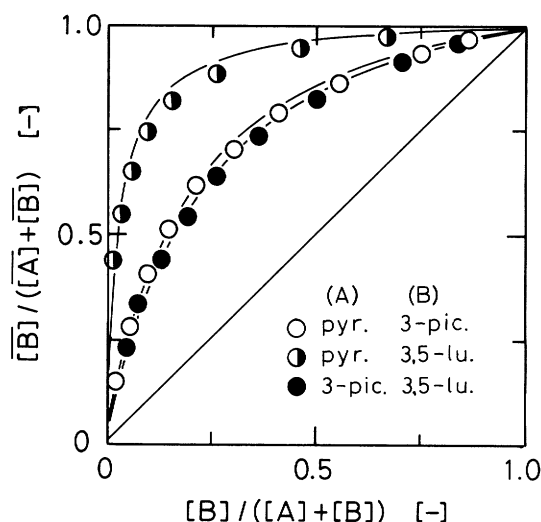
The equilibrium relations on both H-forms 200C

Fig. 6 Relationship between fractional concentrations of pyridines in aqueous and resin phases for sorption on XAD-4. Pyr., 3-pic. and 3,5-lu. represent pyridine, 3-picoline and 3,5-lutidine respectively.

Table 4. Separation factors for the binary systems in the sorption of pyridines

Resin	Adsorbate A	Adsorbate B	$[A]_0 + [B]_0$ (mol/dm³)	$W \times 10^3$ (kg)	α (-)
XAD-4	pyr.	3-pic.	0.01	0.250	6.08
	pyr.	3, 5-lu.	0.01	0.250	32.95
	3-pic.	3, 5-lu.	0.01	0.250	5.35
200C (H)	pyr.	3-pic.	0.05	0.156	2.18
	pyr.	3, 5-lu.	0.05	0.156	4.01
	3-pic.	3, 5-lu.	0.05	0.156	1.91
IRC-50 (H)	pyr.	3-pic.	0.01	0.167	3.89
	pyr.	3, 5-lu.	0.01	0.167	14.41
	3-pic.	3, 5-lu.	0.01	0.167	3.75

and IRC-50 had the same trend as on XAD-4, though having much smaller selectivity. The value of α are also given in Table 4. The separation of pyridine derivatives on the ion-exchange resins may be mainly caused by the difference in basicity of the pyridines, since the sorption is based on the neutralization reaction. As Table 4 shows, the separation factors for the H-form 200C depend on the differences in pKa of the two solutes relevant to each binary system; the same sequence in the separation factors is also observed for the H-form IRC-50. Furthermore, it is evident from Table 4 that the separation factors for weak acid IRC-50 have much higher values than do those for the strong acid 200C.

Conclusion

Sorption equilibria of pyridine derivatives on two ion-exchange resins and four porous resins were studied in terms of the sorption isotherm and separation factor. The following results were obtained.

1) The sorption behaviors of pyridines on the strong acid ion-exchange resin were expressed by the Langmuir iso-

therms, and those on the weak acid ion-exchange and porous resins by the Freundlich isotherms.

2) Methanol content of the aqueous media as well as pH had significant effects on the sorptibilities of these resins. A criterion for selection of the regenerants was presented.

3) The selective sorption of pyridines increased in the following sequences: pyridine < 3-picoline < 3, 5-lutidine; among the three resins: 200C < IRC-50 < XAD-4.

Nomenclature

C	=	concentration in the aqueous phase	[mol/dm³]
q	=	concentration in the resin phase	[mol/kg]
V	=	volume of aqueous phase	[dm³]
W	=	dry weight of the resin	[kg]
α	=	separation factor	[–]
[ ]	=	concentration in the aqueous	
		or resin phase	[mol/dm³], [mol/kg]

\<Subscript\>
0   = initial

\<Superscript\>
—   = resin phase

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