

## Uptake of Iodine and Bromine by Ion-Exchange Resins in Aqueous Solution

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The uptakes of molecular iodine and bromine by both strong acid cation (Dowex 50W-X4 and X8) and strong base anion (Dowex 1-X4 and X8) exchange resins have been studied in aqueous solutions at 25°C. An empirical formula for the amount of solute taken up by the resin in mmol per gram of dry resin,  $Q$ , as a function of the solute concentration in M (mol dm<sup>-3</sup>),  $C$ , was derived. Direct proportional relationships between  $Q$  and  $C$  have been found, except for the bromine-anion exchanger system. In contrast to the cation-exchange resin, the anion exchanger exhibits extremely high affinity for I<sub>2</sub> and Br<sub>2</sub>.

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We recently studied the uptake of alkanes and alcohols,<sup>1</sup> cycloalkanes and bicyclic aromatic compounds,<sup>2</sup> as well as benzene and alkylbenzenes<sup>3</sup> by ion-exchange resins from aqueous solutions. We demonstrated that the uptake of these solutes is governed by partition, rather than adsorption. The distribution constants of these organic nonelectrolytes have been found to increase with the octanol-water partition coefficient. Our present concern is to elucidate the uptake characteristics of inorganic nonelectrolytes by ion-exchange resins.

It has been reported by many workers that polyiodide ions, such as triiodide and pentaide, exhibit extremely high affinity for quaternary ammonium strong-base anion-exchange resins in aqueous solutions.<sup>4,5</sup> The triiodide resin is now being used as a disinfectant for water. For this use, attempts have been made to release the controlled low levels of iodine from anion resins, to which iodine molecules are strongly retained.<sup>6</sup> The extremely high affinity of molecular iodine for anion-exchange resins was first reported in 1953 by Sekino,<sup>7</sup> who found that, in obtaining iodide and iodine from subterranean brine using anion-exchange resins, free iodine liberated by the oxidation of iodide was molecularly adsorbed on resin particles *in situ*.

It is interesting to compare the uptake behavior of organic nonelectrolytes with that of inorganic molecular species in aqueous solutions in the presence of ion-exchange resins. Here, we employed iodine and its homolog, bromine, as inorganic solutes. The affinity of bromine for anion-exchange resins was also discussed by Sekino,<sup>7</sup> though quite briefly.

## Experimental

### Materials

Ion-exchange resins of 100 to 200 mesh used in this study, Dowex 50W (Cl<sup>-</sup> form) and Dowex 1 (H<sup>+</sup> form), and their conditionings were described previously.<sup>1-3</sup> Iodine and bromine were of analytical grade, commercially available from Wako Pure Chemical Co., and were used as received.

### Measurements of solute uptake by resins

When iodine was used as a solute, a vapor-circulation technique described in previous papers<sup>3,8</sup> was used to prepare aqueous solutions saturated with the solute. The iodine solute vapor was generated by bubbling air through a cylindrical separatory funnel, in which an excess amount of solid iodine was placed together with water. The vapor was dispersed *via* a glass capillary through an aqueous solution of *ca.* 100 cm<sup>3</sup> at 25°C, to which ion-exchange resin particles of 2 to 10 g for the cation exchanger, or 0.5 to 1 g for the anion exchanger, were added in advance. The vapor was circulated in a closed system for a prescribed time to reach equilibrium: *ca.* 1 h for cation exchangers and *ca.* 3 to 5 h for anion exchangers. It can be easily judged by observing the color of the aqueous phase to attain equilibrium.

After equilibrium had been reached, the aqueous solution containing the cation exchanger was transferred to a centrifuge tube of 10 cm<sup>3</sup> capacity. The supernatant was removed and a 5-cm<sup>3</sup> portion of cyclohexane was added. Then, the stoppered centrifuge tube was vigorously hand-shaken, and finally centrifuged for 10 min at 3000 rpm. Absorption of the cyclohexane phase was measured at 528.5 nm. The content of the centrifuge tube after an absorption measurement was transferred to a sintered glass filter, and the recovered resin particles were washed with water by suction. A glass filter with resin was dried at 80°C and weighed.

As for anion exchangers, an aqueous solution containing resin particles of *ca.* 100 mg was transferred to a sintered glass filter. A few drops of a commercially available sulfurous acid solution (*ca.* 5% as SO<sub>2</sub>) and a 1 M NaCl solution were added to the glass filter to elute iodine in the form of iodide from the anion-exchange resin. The filtrate was diluted with distilled water, and its known volume was treated with 0.5 cm<sup>3</sup> of H<sub>2</sub>SO<sub>4</sub> (1 + 1) and 1 cm<sup>3</sup> of 3% H<sub>2</sub>O<sub>2</sub> to oxidize iodide to iodine, followed by extraction with cyclohexane and by an absorption measurement. The glass filter with the resin was dried at 80°C and weighed.

When bromine was used as a solute, the vapor-circulation technique was not applicable to such a highly volatile solute. Then, another technique was employed.<sup>3</sup> A glass test tube with a glass stopper of *ca.* 30 or 100 ml capacity was filled with an aqueous solution saturated or unsaturated with bromine. The

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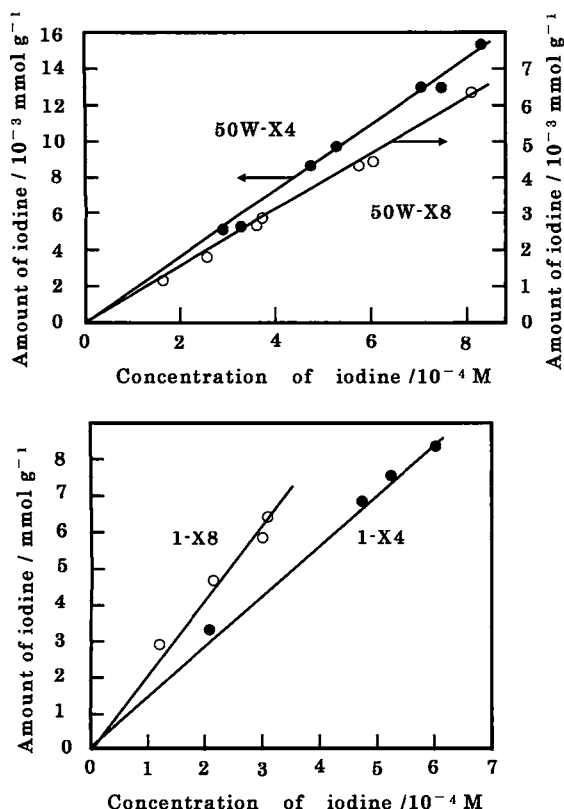


Fig. 1 Amount of iodine taken up by cation-exchange resins (upper) and anion-exchange resins (lower) against the concentration of iodine in an aqueous solution in equilibrium with resins.

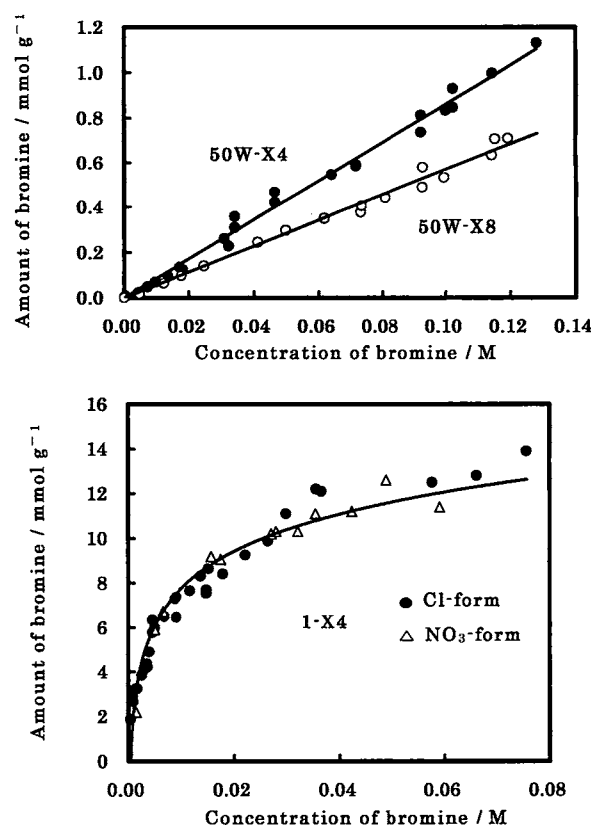


Fig. 2 Amount of bromine taken up by cation-exchange resins (upper) and anion-exchange resins (lower) of Cl<sup>-</sup> form and NO<sub>3</sub><sup>-</sup> form.

saturated bromine solution was prepared by adding an excess amount of liquid bromine to water. A suitable amount of resin was placed into a test tube, which was immersed in a bath thermostated at 25°C for *ca.* 30 min for cation exchangers and days for anion exchangers with occasional shaking.

The other procedures used to estimate bromine uptakes by cation and anion exchangers were carried out in the same way as iodine, except for using carbon tetrachloride instead of cyclohexane as the extracting solvent. The absorption of bromine in carbon tetrachloride was measured at 415.5 nm. The concentrations of iodine and bromine in equilibrium with resins were determined by absorption measurements after extracting supernatant aqueous solutions with cyclohexane for iodine and carbon tetrachloride for bromine.

## Results and Discussion

The amounts of solute taken up by resins, expressed in mmol per gram of dry resin ( $Q$ ), are plotted against the solute concentration ( $C$ ) in equilibrium with the resin in M in Figs. 1 to 3. In Table 1 are summarized the formulae of  $Q$  as a function of  $C$ . From these results we can see the following three points:

- (1) The amount of iodine taken up by both cation- and anion-exchange resins and that of bromine by cation exchangers were directly proportional to the solute concentration in the aqueous solution, while this was not the case for the bromine-anion exchanger system.
- (2) The distribution constants ( $K$ ), which correspond to the hypothetical solute amount (mmol/g of dry resin) at an aqueous solute concentration of 1 M, are significantly higher

for anion exchangers than for cation exchangers.

- (3) The amount of bromine taken up by the Cl<sup>-</sup> form anion exchanger was in good agreement with the NO<sub>3</sub><sup>-</sup> form resin in the range of the aqueous bromine concentration studied.

All of the organic nonelectrolytes that we have so far studied have shown a direct proportional relationship between the amount of solute taken up by resins and the solute concentration in aqueous solutions.<sup>1-3</sup> This gives us an image of solvent extraction, the partition of a solute between the organic solvent and the aqueous phase; resin particles seem to be an organic solvent. In the present study, however, the uptake mechanism of the bromine-anion exchanger system appeared to be adsorption rather than partition.

In an attempt to obtain some information about the uptake mechanism by anion-exchange resins, we examined microscopically, as described in a previous paper,<sup>2</sup> using relatively large resin particles (Dowex 1-X4, Cl<sup>-</sup> form, 20 - 50 mesh). Vertical sectional views are shown in Fig. 4. Resin particles prepared in an aqueous bromine solution of *ca.* 0.02 M for 1 h (a) and for 1 day (b) appeared to be uniform in reddish-brown color throughout a resin particle; the color was deeper for prolonged contact. It should be mentioned that vertical sectional views were all the same for iodine, and that resins prepared under high bromine aqueous solutions or after prolonged contact-times with aqueous iodine solutions were found to be too rigid to be cut with a razor to see their vertical sectional views.

On the other hand, the resins prepared under conditions that they had been placed in a sealed container together with a saturated bromine aqueous solution separated in space for 1 day

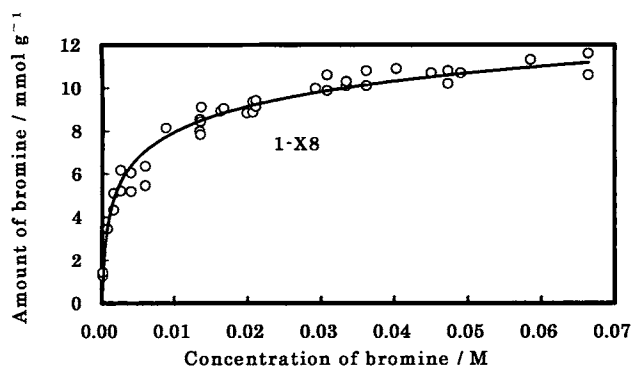


Fig. 3 Amount of bromine taken up by anion-exchange resin of the  $\text{Cl}^-$  form.

(c) and for 1 week (d) indicated that the colored zone gradually proceeded from the outside to the inner part. This is analogous to the situation observed in our previous work,<sup>2</sup> where an anionic dye (Acid Red 1) was adsorbed on an anion-exchange resin in an aqueous solution.

We first expected that, if bromine molecules were adsorbed on the anion-exchange resins in aqueous solutions, the vertical sectional views might be similar to those prepared in the air circumstances. Microscopic examinations, however, seem to support that the uptake of dissolved bromine by the anion-exchange resin is governed by partition.

It can be seen from Fig. 2 (lower) and Fig. 3 that the anion-exchange resins are nearly saturated with bromine, even at an aqueous bromine concentration range considerably lower than in the case of cation exchangers. Uptake runs in the presence of anion resins were planned to carry out at lower bromine concentrations, but the bromine concentrations in the aqueous phase were too small to detect.

As has been shown by many workers, anion-exchange resins exhibit strong affinity for iodine, and also for bromine. The distribution constants ( $K$ ) for cation-exchange resins are small: 18.1 for X-4 and 7.70 for X-8 (see Table 1). These  $K$  values fall within the line expected from  $K_{\text{ow}}$ .<sup>3</sup> The  $K_{\text{ow}}$  value of iodine was determined in this work to be 270, while that of bromine was not determined, because a denaturant of bromine occurred during shaking with the aqueous octanol phase. On the other hand, the  $K$  values of iodine for anion-exchange resins,  $1.39 \times 10^4$  for X-4 and  $1.89 \times 10^4$  for X-8, are extremely higher than expected from the  $K_{\text{ow}}$ ; even higher than those of bicyclic aromatic compounds, such as naphthalene, biphenyl and azulene, the  $K$  values of which are relatively high due to the  $\pi$  interaction of aromatic rings with the resin matrix.<sup>2</sup>

Hatch *et al.* have suggested that the high affinity of the triiodide ion for the quaternary ammonium anion-exchange resin is due to a synergistic stabilization through interactions of triiodide ion with the positively charged quaternary ammonium site and the localized aromatic ring in the resin.<sup>5</sup> Sekino, on the other hand, has proposed that iodine molecules are attracted to the amino-groups of the anion resin due to mutual polarities: the intermolecular charge-transfer interaction of electron-accepting iodine and basic nitrogen in the amino-group.<sup>7</sup>

There are possibilities that heteronuclear trihalide anions,  $\text{X}_2\text{Y}^-$  ( $\text{X}, \text{Y} = \text{Cl}, \text{Br}, \text{or I}$ ), may be formed<sup>9</sup> and such trihalide anions may result in the high affinity for anion-exchange resins. Thus, bromine uptake runs were carried out using the  $\text{NO}_3^-$  form resin. The results shown in Fig. 2 (lower) indicate no appreciable difference between the  $\text{Cl}^-$  and  $\text{NO}_3^-$  forms. Sekino

Table 1 Empirical formula of the amount of solute taken up by resins in mmol per gram of dry resin ( $Q$ ) as a function of the solute concentration in M ( $C$ ) at  $25^\circ\text{C}$ <sup>a</sup>

Solute	Dowex 50W		Dowex 1	
	X4	X8	X4	X8
Iodine	$Q = 18.1C$ (0.994)	$Q = 7.70C$ (0.998)	$Q = 1.39 \times 10^4 C$ (0.994)	$Q = 1.89 \times 10^4 C$ (0.999)
Bromine	$Q = 8.62C$ (0.991)	$Q = 5.71C$ (0.987)	$Q = 2.41 \ln C$ + 18.9 <sup>b</sup> (0.941)	$Q = 1.70 \ln C$ + 15.8 <sup>c</sup> (0.965)

a. Correlation coefficients are shown in the parentheses.

b.  $C$  should be larger than  $6.0 \times 10^{-4}$  M.

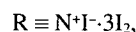
c.  $C$  should be larger than  $2.0 \times 10^{-4}$  M.

also showed in his iodine uptake runs that there was no appreciable difference between the  $\text{Cl}^-$  and  $\text{I}^-$  form resins.<sup>7</sup>

Sekino has described in his pioneering paper that iodine molecules are adsorbed on the anion-exchange resin according to the Freundlich adsorption isotherm.<sup>7</sup> This is not in agreement with our present results: Fig. 1 (lower) and microscopic observations indicate partition rather than adsorption. The difference between the two studies may be ascribed to the different techniques employed to prepare resins associated with iodine. While we used only molecular iodine dissolved in water, Sekino used aqueous iodine solutions mixed with a certain amount of  $\text{KI}$ ,<sup>7</sup> where some ion-exchange contributions from  $\text{I}_3^-$  may be concerned with the uptake equilibrium.

He has also stated that a 1-g portion of dry resin, Amberlite IRA-400 (quaternary ammonium type), adsorbs *ca.* 2 g (7.9 mmol) of free iodine.<sup>7</sup> This value, though the cross-linking data of his resin were not specified, is in fairly good agreement with the present result, Fig. 1 (lower). If we postulate, however, that the linear relationship holds up to the aqueous solution saturated with iodine,  $12.1 \times 10^{-4}$  M,<sup>8</sup> the amount of iodine taken to Dowex 1-X4 amounts to 16.8 mmol (4.3 g), and Dowex 1-X8 to 22.9 mmol (5.8 g). Moreover, based on his preliminary runs, Sekino reported with reservations that a 1-g of dry Amberlite IRA-400 adsorbs *ca.* 9 mmol of bromine,<sup>7</sup> which is comparable to the present results (Figs. 2 and 3).

Sekino<sup>7</sup> explained the amount of iodine taken up by the anion-exchange resin to an extent even beyond several times the ion-exchange capacity by considering that the basic nitrogen atom in the anion-exchange resin attracts one iodine molecule firmly. The other iodine molecules are polarized and loosely attracted to the amino-group of the resin. He proposed the following uptake formula:



where  $\text{R} \equiv \text{N}^+$  represents an anion resin of the quaternary amine type, and  $\text{I}^-$  refers to the exchange-adsorbed iodide ion. He postulated that up to three iodine molecules can be adsorbed per one amino group.<sup>7</sup>

Some aliphatic acids at higher concentrations have been reported to exhibit high affinity for the strong base anion-exchange resin beyond its ion-exchange capacity.<sup>10</sup> This is probably due to the contribution from the undissociated aliphatic acid, that is, partition of these hydrophobic undissociated species between the resin and the aqueous phase.

Our present work indicates that uptakes of iodine (and probably bromine) to both cation- and anion-exchange resins are

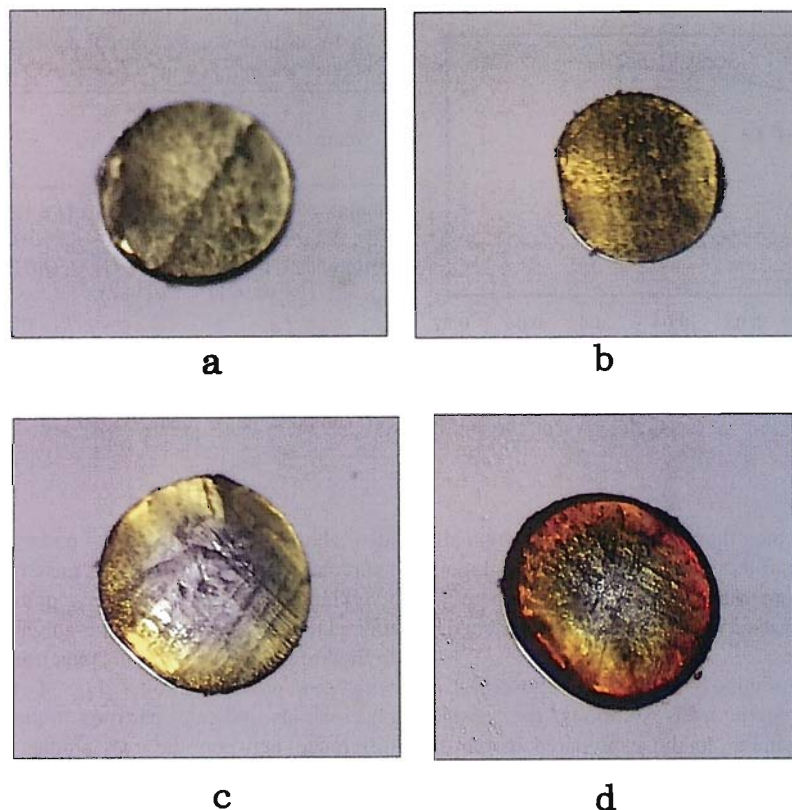


Fig. 4 Microscopic vertical sectional views (magnification 60 times) of resin particles (Dowex 1-X4, 20-50 mesh,  $\text{Cl}^-$  form) after contact with aqueous bromine solutions of ca. 0.02 M for 1 h (a) and for 1 day (b); after being allowed to stand to the vapor of bromine for 1 day (c) and for 1 week (d).

governed by partition rather than adsorption. The  $K$  value of iodine for the cation-exchange resin falls within the line expected from  $K_{ow}$  observed for organic nonelectrolytes, while that for the anion-exchange resin highly deviates from the line. There have been proposed two different mechanisms concerning specific affinity of iodine for the quaternary ammonium anion-exchange resin: the interaction of iodine with basic nitrogen in the amino group in the resin proposed by Sekino,<sup>7</sup> or with the localized aromatic ring in the resin proposed by Hatch *et al.*<sup>5</sup> We cannot conclude here which is more reasonable.

The effect of cross-linking of the resin on the uptakes of iodine and bromine is consistent with our previous data.<sup>1-3</sup> The lower cross-linking is favorable for the cation exchanger. This is probably due to the decrease in the solute migration resistance in the resin phase. On the other hand, the higher cross-linking is favorable for the anion exchanger to contact more tightly with solute molecules.

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