Perchlorate Selectivity of Anion Exchange Resins as Evaluated Using Ion-Selective Electrodes

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The selectivity coefficients reported for perchlorate of the high selectivity on anion exchange resins (AXRs) have not been consistent with one another. Possible errors by the unique use of four parameters (concentrations of two anions in two phases) were experimentally verified. The concentrations of perchlorate buffered at low levels (10⁻⁶ – 10⁻⁴ mol L⁻¹) by two forms of AXRs were successfully determined by potentiometry with a perchlorate ion-selective electrode. This gave reasonable coefficients. The coefficients for perchlorate on several AXRs were independent of the relative exchange (RE), in contrast to the previous reports. On the other hand, the coefficients for fluoride of the low selectivity that were examined for comparison decreased with an increase in RE, and the dependency was more remarkable for the resins of large exchange capacity.

Keywords Anion exchange resin, perchlorate, selectivity coefficient, ion-selective electrode

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Introduction

Perchlorate as a contaminant in groundwater and surface water has attracted attention because of its adverse effects such as inhibition of iodide uptake and endocrine-disruption.¹² Ion-exchange resin technology is believed to be promising for removal of perchlorates in water. From the practical viewpoint, new resins and technologies have been developed for the purpose of achieving rapid exchange, enhancing the sorption capacity, allowing for desorption of perchlorate and reuse of the resin, and decomposing perchlorate in the resin phase.³⁻⁹

Fundamental information, however, has been limited. For example, only one of these papers described the most important parameter of the selectivity coefficient; log $K_{clO_4^{-}}$: 2.72 for QPEI-4 (hyperbranched polyethyleneimine-type resin), 2.78 for A-530E (styrene divinylbenzene-type resin).⁹ The coefficients of varying anions on the conventional resins were independently studied by several groups in the 1950s¹⁰⁻¹³ and later.¹¹,¹⁵ These values were in reasonable agreement with each other except for perchlorate, for which extremely different values were reported: for example, log $K_{clO_4^{-}}$: 2.18 and 1.5 for type I (with trimethylaminomethyl group, cross-linking of 8%);¹²,¹³ 1.4 for type II (with 2-hydroxyethylidimethylamine-methyl group).¹¹ Even a variation in selectivity coefficient according to the relative exchange was suggested and discussed.¹¹,¹³,¹⁴,¹⁷ Under such circumstances, a recent paper described the coefficient only at the molar fraction of ClO₄⁻ of 10⁻⁴ level in the resin phase.¹⁸ The modern handbooks do not include the coefficient for perchlorate, which leads to inconsistency of literature data, from the experimental points of view. We have successfully reevaluated the selectivity coefficients of perchlorate on the resins of different exchange capacities, cross-linking degrees, and basicities by potentiometry with an ion-selective electrode (ISE). The coefficients of other typical anions of lower affinities (fluoride, chloride, and nitrate) were also determined by ion chromatography (IC), and the dependency of the coefficient on the composition of the resin phase has been discussed.

Experimental

Reagents and chemicals

Four strongly basic anion exchange resins (SBAs) and four weakly basic anion exchange resins (WBAs) were evaluated. Among them, three SBAs and one WBA were commercially available (Dowex 1×2, Dowex 1×8, Dowex 2×8, and Dowex WBA abbreviated as I-3×2, I-3×8, II-2×8, and W-4, respectively; the first digit denotes an approximate exchange capacity and the second digit, if applicable, denotes the cross-linking degree by divinylbenzene; macroporous), while the gel-type resin of a low exchange capacity with trimethylaminomethyl group (I-1×2) and those with dimethylamino group (W-1, 2, 3) were derived from the Merrifield resins (TCI, Cl contents/mmol g⁻¹, cross-linking: 0.9; 2%; 1.9; 2%; 2.9; 1%) as described previously.²⁰,²¹ Introduction of the ammonium or amino group was confirmed by the decrease in IR absorption around 1265 cm⁻¹ due to H-C-Cl stretching.²² The IR spectra showed that only W-4 among WBAs had strong broad absorption centered at 3450 cm⁻¹ with a half-height width of 300 cm⁻¹; this suggests the presence of some hydrophilic group. Each of the SBAs was treated with a NaCl or NaBr solution by a flow system to be determining the coefficient for perchlorate, which leads to inconsistency of literature data, from the experimental points of view. We have successfully reevaluated the selectivity coefficients of perchlorate on the resins of different exchange capacities, cross-linking degrees, and basicities by potentiometry with an ion-selective electrode (ISE). The coefficients of other typical anions of lower affinities (fluoride, chloride, and nitrate) were also determined by ion chromatography (IC), and the dependency of the coefficient on the composition of the resin phase has been discussed.

In this study, we first demonstrated the difficulty in determining the coefficient for perchlorate, which leads to inconsistency of literature data, from the experimental points of view. We have successfully reevaluated the selectivity coefficients of perchlorate on the resins of different exchange capacities, cross-linking degrees, and basicities by potentiometry with an ion-selective electrode (ISE). The coefficients of other typical anions of lower affinities (fluoride, chloride, and nitrate) were also determined by ion chromatography (IC), and the dependency of the coefficient on the composition of the resin phase has been discussed.

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The Cl– or Br– content in the supernatant was determined. The accurately calculated exchange capacity of SBA is summarized in Table 1. The appreciable difference in exchange capacity between Br-form and Cl-form for II-2 is attributable to the difference in molecular weight between Br– and Cl– and the difference in their hydration numbers as published previously.21

Table 1  Properties of SBAs and WBAs as free base

| SBA, form | Type | Origin | Exchange capacity/ mmol g–1 | n° |
|-----------|------|--------|-----------------------------|---|
| I-1×2, Br– | Gel | a | 0.77 ± 0.03 | 10 |
| I-3×2, Br– | Porous Dowex 1×2 | | 3.17 ± 0.02 | 9 |
| I-3×8, Br– | Porous Dowex 1×8 | | 2.76 ± 0.02 | 9 |
| II-2×8, Br– | Porous Dowex 2×8 | | 2.18 ± 0.02 | 4 |
| II-2×8, Cl– | Porous Dowex 2×8 | | 2.58 | 1 |

| WBA | Type | Origin | Nitrogen content/ mmol g–1 | Water content, % |
|-----|------|--------|---------------------------|-----------------|
| W-1 | Gel | a | 0.84 | 0.1 |
| W-2 | Gel | a | 2.02 | 0.2 |
| W-3 | Gel | a | 2.77 | 0.4 |
| W-4 | Porous Dowex WBA | | 4.19 | 2.9 |

a. Derived from Merrified resin.
b. Number of data.

Since the four parameters, [X–], [A–], [-R+,X–] and [-R+,A–] are related to each other by Eqs. (2) - (4), the coefficient $K_{X^A}$ may be calculated from only one of them by Eqs. (5) - (8):

$$K_{X^A} ([X–]) = ([X–] q) / (TAX – [X–] q)$$

(5)

$$K_{X^A} ([A–]) = (TAX – [–R+,X–] q) / ((TAX – [X–] q)([A–] q))$$

(6)

$$K_{X^A} ([–R+,X–]) = (TAX – [-R+,X–] m) / (((–R+,X–) q)(TAX – [X–] q)$$

(7)

$$K_{X^A} ([–R+,A–]) = ([–R+,A–] m) / ((TAX – [–R+,A–] m)(TAX – [–R+,A–] m))$$

(8)

The relative exchange (RE) of X– on the resin by A– is also calculable from one of four parameters by Eqs. (9) - (12):

$$RE([X–]) = ([X–] q) / (TAX)$$

(9)

$$RE([A–]) = (TAX – [–R+,X–] q) / (TAX)$$

(10)

$$RE([-R+,X–]) = (TAX – [-R+,X–] m) / (TAX)$$

(11)

$$RE([-R+,A–]) = ([–R+,A–] m) / (TAX)$$

(12)

Reliable analysis needs to observe the RE in the range of 0.1 to 0.9, which corresponds to the range of 3 to 4 in $\log[A–]$. Suitable analytical method is required, depending on the property and the concentration of the relevant anion.

Procedure

SBAs of 10 to 100 mg (Cl-form of II-2×8 for exchange by NO₃– and Br–; Br-forms for the others) were shaken with a series of sodium salt solutions of relevant anions (25 mL of 10⁻¹.⁵ – 10⁻¹.⁰ mol L⁻¹; chemicals amount ratio of anion to ion-exchange capacity = 0.3 – 100). After equilibration, the resins were filtered off and were shaken with NaClO₄ solutions to elute anions in the resin phase.

In the case of WBAs (~N), coadsorption of strong acids (HA: HClO₄, HNO₃, HBr or HCl; HF was not included because of experimental difficulty) given by Eq. (13) was first evaluated.

$$-N + H^+ + A^– = (-NH+,A–)$$

(13)

Based on the results, 10 to 100 mg neutral base resins were shaken with a series of mixtures of two acids with the total concentration kept at 10⁻² mol L⁻¹. In the presence of proton at 10⁻² mol L⁻¹, the free bases of WBAs except W-1 became wet and were protonated to have ion exchange ability. After equilibration, the resins were filtered off and were shaken with NaClO₄ solutions to elute anions.

The supernatants and the eluents were subjected to IC with conductometric detection. The condition (eluent of 8 mmol L⁻¹ p-hydroxybenzoic acid and 2.8 mmol L⁻¹ Bis-Tris, pH 3.6) was suited for the determination of F–, Cl–, Br– and NO₃– but not for that of ClO₄– because of serious broadening of the peak.

Perchlorate ISE was prepared as described previously using tri(dodecyl)methylammonium chloride and was conditioned in a 10⁻² mol L⁻¹ NaClO₄ solution before use.23 The potential of the following cell kept at 25°C was used for the potentiometric determination of ClO₄⁻:
Results and Discussion

Evaluation of selectivity coefficients with four parameters

Preliminarily, four parameters [X¹], [A¹], [-R·X¹] and [-R·A¹] involved in the exchange of the Br-form of I-3×8 by CNO⁻ (X⁻: Br⁻; A⁻: CNO⁻) were determined by a versatile apparatus of IC, and all the four types of $K_{s}^{CNO}$ and RE were calculated with a view to enhancing the reliability of and focusing on the difficulty in the evaluation. As shown in Fig. 1, the coefficients were in good agreement with one another, except $K_{s}^{CNO}$([-R·CNO⁻]) that was plotted against RE([-R·CNO⁻]). The deviation of $K_{s}^{CNO}$([-R·CNO⁻]) was attributed to the unique partial decomposition of CNO⁻ in the elution step as verified by the appearance of other peaks in ion chromatography.

At the high RE (≥0.8) where [-R·Br⁻] became small, $K_{s}^{CNO}$([Br⁻]) and $K_{s}^{CNO}$([CNO⁻]) (omitted) could not be evaluated properly, because of unreliable estimates of [-R·Br⁻] from [Br⁻] and [CNO⁻], respectively. Only direct measurement of [-R·Br⁻] after elution gave reasonable results at the high RE.

In summary, any parameters can be used to evaluate the coefficient for anions of moderate selectivity at RE = 0.2 - 0.8.

Selectivity coefficients of ClO₄⁻ with use of ion selective electrode

The supernatant in exchange of the Br-form of I-3×8 by ClO₄⁻ (X⁻: Br⁻; A⁻: ClO₄⁻) was subjected to IC for the purpose of determining [Br⁻]. Unless a special column and eluent were adopted, $K_{s}^{ClO4}$ could not be determined by IC. Thus, neither $K_{s}^{ClO4}$([ClO₄⁻]) by Eq. (6) nor $K_{s}^{ClO4}$([-R·ClO₄⁻]) by Eq. (8) was obtained in this study. The $K_{s}^{ClO4}$([Br⁻]) plotted in Fig. 1 shows an increase with an increase in RE, but this is not reliable since the anion of the high selectivity, ClO₄⁻, almost quantitatively exchanges Br⁻ in the resin. For example, in the case of exchange of 10 mg of I-3×8 by ClO₄⁻ at 2.00 and 4.00 × 10⁻⁸ mol L⁻¹, the bromide concentration determined was 1.93 and 3.78 × 10⁻⁴ mol L⁻¹, respectively. [ClO₄⁻] calculated from the difference, 0.07 and 0.22 × 10⁻⁴ mol L⁻¹, suffered from a large positive error. Thus, $K_{s}^{ClO4}$([Br⁻]), if available, systemetically suffered from a negative error. This trend is more remarkable at the low RE on low loading.

Under such conditions, [ClO₄⁻] is, in a sense, buffered at a low concentration level (10⁻⁸ - 10⁻⁴ mol L⁻¹ level) by a pair of [-R·ClO₄⁻] and [-R·Br⁻], and separation of the supernatant from the resin is prone to suffer from a large error in quantitation as in the case of pH measurement of a neutral solution in the absence of a pH buffer. Although a special ion chromatographic system with a ClO₄⁻ detection limit of 2 ppb = 2 × 10⁻⁷ mol kg⁻¹ was used in the recent paper, in situ determination of [ClO₄⁻] in the presence of both types of resins is preferable. Potentiometry of perchlorate with ISE responding to the logarithmic concentration is suitable in these respects just as potentiometry of proton with a glass electrode is suited for pH determination of buffered solutions.

The $K_{s}^{ClO4}$([ClO₄⁻]) using [ClO₄⁻] determined by ISE is also plotted in Fig. 1. The $K_{s}^{ClO4}$([ClO₄⁻]) value was independent of RE in contrast to the previous paper, and was close to the $K_{s}^{ClO4}$([Br⁻]) value using [Br⁻] by IC at the high RE. This is because the error in $K_{s}^{ClO4}$([Br⁻]) described above is less at the high RE. These results are consistent with each other, so that both the inconsistency and the RE dependency of $K_{s}^{ClO4}$ in the previous work are attributed to the inappropriate anion determination in the supernatant. The $K_{s}^{ClO4}$ value of 10²⁻¹⁸ calculated from the difference between $K_{s}^{ClO4}$ and $K_{s}^{Br}$ agreed well with that determined by radiometry.

Potentiometry with ISE is effective and is generally applicable to evaluation of $K_{s}^{Br}$ for the anions A⁻ of the high selectivity.

Selectivity coefficients of fluoride

The RE dependencies of the selectivity of four anions on four SBAs are shown in Fig. 2. The coefficients of anions except F⁻ were independent of RE on any resins. The log $K_{s}^{F}$ values on I-1×2, I-3×8 and I-3×2, on the other hand, decreased with an increase in RE from 0 to 100% by 0.30, 0.34, and 0.43, respectively (Figs. 2a, 2b, 2c). Fluoride is extremely hydrophilic and is appreciably hydrated even in the resin phase. The enhanced swelling of the resin at the high RE by F⁻ is resisted by cross-linking to decrease the F⁻ selectivity. Such a decrease was more remarkable for the resin of the large exchange capacity. A similar decrease was observed for the other hydrophilic anions of carboxylates.

The resin of II-2×8 has a hydroxyethyl group, which is likely to serve as a hydrogen-bond donor and interact with F⁻. The hydration number of F⁻ on II-2×8 (4.8) determined as described previously was actually smaller than that on I-3×8 (5.6) by around unity. As a result, swelling was relieved and the selectivity was kept substantially constant with an increase in RE on II-2×8 (Fig. 2d).
Coadsorption of acids to and selectivity coefficients on WBAs

The stoichiometric amounts of H+ and A– (equal to the chemical amount of the dimethylamino group) were coadsorbed to W-4 at a total acid concentration of greater than 10^{-2} mol L^{-1}, while no coadsorption was observed for W-1 because of low wettability. In the case of W-2 and W-3, stoichiometric coadsorption was observed only for HNO_3, HBr, and HCl after a long equilibration time of around one week, but HClO_4 was coadsorbed only up to several tens of percent at the maximum. Based on these findings, the selectivity coefficients were evaluated for the combination of the acids of quantitative coadsorption as described in the experimental section. The selectivity coefficients were also independent of RE (Tables S17 – 23, Supporting Information).

Comparison of resins

The selectivity coefficients of four anions on four SBAs and those of two or three anions on three WBAs are summarized in Table 2 and are compared in Fig. 3, where the values at RE = 0.5 are taken for log $K_{BrA}$ of I-1×2, I-3×8 and I-3×2. The difference between log $K_{BrClO_4}$ and log $K_{BrF}$ of trimethylaminomethyl-type SBAs decreased in the order of I-1×2(3.99) > I-3×8(3.34) > I-3×2(2.29). The resin of I-1×2 contains an appreciable amount of styrene without an ammonium group and provides a more lipophilic or less hydrophilic environment. Thus, a lipophilic anion is more favorably exchanged, while a hydrophilic anion is more poorly exchanged. In contrast, I-3×2 affords the more hydrophilic environment and loses the differentiating ability by as much as 1.7 in logarithmic scale. The resin of I-3×8 is less flexible than I-3×2 and shows the intermediate ability. The resin of II-2×8 showed the higher selectivities to the anions of the hydrogen bond acceptor, such as fluoride and nitrate, compared with I-3×8. WBAs also showed the higher selectivities to the nitrate of the hydrogen bond acceptor; this trend was more remarkable for the resins of the lower nitrogen content as in the cases of SBAs.

Conclusions

Perchlorate is almost quantitatively exchanged when in contact with anion exchange resins. Under such conditions, [ClO_4^–] buffered at the low level in the supernatant was successfully determined by potentiometry with ISE to give a reasonable selectivity coefficient. This method is generally applicable to any lipophilic anions.

Table 2 Logarithmic values of selectivity coefficients ($K_{BrA}$) of four anions on seven resins

| Resin | ClO_4^- | NO_3^- | Cl^- | F^- |
|-------|---------|--------|------|-----|
| I-1×2 | 1.91 ± 0.03 (6) | 0.13 ± 0.02 (5) | -0.70 ± 0.00 (6) | -1.93 ± 0.30 × RE (8) |
| I-3×8 | 1.61 ± 0.03 (14) | -0.1 ± 0.1 (5) | -0.60 ± 0.05 (7) | -1.55 ± 0.34 × RE (7) |
| I-3×2 | 1.32 ± 0.05 (8) | -0.03 ± 0.03 (6) | -0.36 ± 0.01 (4) | -0.75 ± 0.43 × RE (5) |
| II-2×8 | 1.68 ± 0.04 (9) | 0.02 ± 0.02 (7) | -0.53 ± 0.04 (7) | -1.2 ± 0.1 (7) |
| W-2 | n.d.a | 0.31 ± 0.03 (4) | -0.44 ± 0.05 (5) | n.e.c |
| W-3 | n.d.a | 0.21 ± 0.02 (6) | -0.49 ± 0.02 (5) | n.e.c |
| W-4 | 1.36 ± 0.04 (15) | 0.10 ± 0.01 (8) | -0.40 ± 0.04 (6) | n.e.c |

* a. Number of samples in parentheses. b. n.d.: not determinable. c. n.e.: not evaluated.
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Supporting Information

Additional tables showing the numerical data on ion exchange. This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

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