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Nonaqueous anion-exchange chromatography I. Role of solvation in anion-exchange resin

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Abstract

Nonaqueous anion-exchange chromatographic selectivity has been studied in methanol (MeOH), acetonitrile (MeCN), *N,N*-dimethylformamide (DMF), and their mixtures. Changing solvents results in drastic changes in anion-exchange selectivity; in MeOH, larger and less solvated ions are more retained, while smaller and more solvated ions are more favorably retained in MeCN or DMF irrespective of the chemical structure of the anion-exchange sites. In solvents with low acceptor ability, the hydrogen bond formation between anions and anion-exchange sites plays a decisive role, and thus the affinity of small anions to the anion-exchange sites comprised of primary ammonium ions is much higher than expected from electrostatic coulombic interaction. In contrast, the affinity to the anion-exchange sites comprised of tetraalkylammonium ions is qualitatively explained by coulombic interaction in the absence of specific adsorption. In most cases, the ratio of k' can be explained by the ratio of the ion-pair formation constants determined in bulk solution, suggesting that ion-pair formation similar to that seen in solution takes place in anion-exchange resins though there is a difference in the absolute values of the equilibrium constant.

Keywords: Ion-exchange selectivity; Mobile phase composition; Electrostatic interactions; Ion-pair formation constants; Stationary phases, LC; Solvation; Inorganic anions

1. Introduction

Principal factors governing ion-exchange selectivity of a simple ion are specific adsorption of ions on ion-exchange resin matrices, the specific ion-pair formation between a counter ion and an ion-exchange resin site (e.g., due to hydrogen bond formation), and nonspecific electrostatic coulombic interaction, although we must take into consideration other interactions, e.g., ion-induced dipole, London dispersion interaction, etc. in any particular case. The first factor can be varied by changing resin matrices, while the second and third factors can be affected by the chemical structure of the ion-exchange sites. The simplest will be the electrostatic interaction because this can be treated by classical electrostatic theories [1–4]. To understand ion-exchange selectivity, we must select systems where the specific adsorption is minimized and the specific ion-pair formation can be quantitatively evaluated. A possible choice to reduce the specific adsorption is the use of organic solvents [5–8], because dispersion forces usually cause the specific adsorption, and since they are eliminated with increasing molecular size and polarizability of the solvents. Though hydrogen bond formation will be enhanced in some organic solvents in comparison to water, this can be evaluated from the corresponding interaction in solution [9].

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Electrostatic coulombic interaction is determined by the balance of the extent of solvation and the strength of the electrostatic field generated around an ion-exchange site [10]. Electrostatic field strength can be usually varied by changing the chemical structure of ion-exchange resin sites. There are a number of reports treating this topic, which lead to the conclusion that a small ion-exchange site with a high charge density (e.g., $-NH_3^+$ for anion separation) produces a stronger electrostatic field than a bulky ion-exchange site with low charge density (e.g., $-NR_3^+$) [11–13]. Under a strong electrostatic field, partial desolvation of counter ions is forced, and thus the ion-exchange selectivity that reflects the crystalline ionic radii appears [13]. In contrast, the radii of solvated ions are reflected in the ion-exchange selectivity under a weak electrostatic field. However, it is generally difficult to quantitatively evaluate the extent of the desolvation of counter ions.

When the ion-exchange selectivity is discussed, our attention is usually focused on the solvation of counter ions and not on the solvation of ion-exchange sites. However, the solvation of ion-exchange sites is also affected by the electrostatic field generated by a counter and the extent of ion-pair formation between an ion-exchange site and a counter ion. Changing solvents will be useful to probe the solvation of both an ion-exchange resin site and counter ion in an ion-exchange resin. The aim of the present paper is to elucidate the relation between solvation and anion-exchange selectivity by varying solvent compositions. We have selected two anion-exchange resins, polymer resins of the same matrix with $-NH_3^+$ and with $-NEt_3^+$ as an anion-exchange site, and four solvents, acetonitrile (MeCN), methanol (MeOH), water (H_2O), and *N,N*-dimethylformamide (DMF), properties of which are listed in Table 1, and their mixtures. MeCN, MeOH, and DMF have almost identical permittivity, but different donor (DN) and acceptor numbers (AN).

Table 1
List of solvent properties

Solvent	ϵ[a]	η[b]/cP	μ[c]/Debye	DN[d]	AN[e]
H_2O	78.3	0.8903	1.85	18.0	54.8
MeOH	32.7	0.5445	1.70	19	41.3
MeCN	35.95	0.3409	3.92	14.1	19.3
DMF	36.71	0.796	3.86	26.6	16

[a] Specific dielectric constant.
[b] Viscosity.
[c] Dipole moment.
[d] Donor number.
[e] Acceptor number.

2. Experimental

The chromatographic system was composed of a Tosoh computer-controlled pump Model CCPD, a Rheodyne injection valve equipped with a 100-μl sample loop, and a Tosoh UV-Vis detector Model UV-8000. A 50 mm×4.6 mm I.D. PTFE separation column was immersed in water thermostated at 25°C.

Stationary phases ($-NH_3^+$ and $-NEt_3^+$) were synthesized by the chloromethylation of MCI 5HP (polystyrene–polyvinylbenzene copolymer, Mitsubishi Chemicals, the mean particle size of which is 5 μm) followed by the reaction with NH3 aqueous dioxane for $-NH_3^+$ resin and with triethylamine (NEt_3) aqueous dioxane for $-NEt_3^+$ resin. Ion-exchange capacities were 0.59 mmol g^{-1} for $-NH_3^+$ resin and 0.37 mmol g^{-1} for $-NEt_3^+$ resin. Changes in the resin volume due to swelling were not observed. To investigate effects of resin matrices, were used silica gel-based ion-exchange resins TSK gel IC-Anion-SW (ion-exchange capacity, 0.4 mmol g^{-1} with 5 μm particle size with $Si\text{-}N(Et)_2Me^+$ as anion-exchange sites) and aminopropylated silica gel ($SiNH_2$), which was synthesized by the reaction of Wakasil 5 Sil (5 μm of particle size and 500 m^2 g^{-1} of specific surface area) with 3-aminopropyltriethoxysilane in dry toluene at room temperature. After packed in the column, the $Si-NH_3^+$ stationary phases were equilibrated with diluted aqueous HCl to allow full protonation. The ion-exchange capacity of the $Si\text{-}NH_3^+$ column was 3.7 mmol g^{-1}.

Water was distilled after deionization. MeOH was refluxed with magnesium and then distilled. MeCN of HPLC grade purchased from Wako Pure Chemicals. DMF was distilled under vacuum after the treatment with molecular sieves for 2 days.

A Toa conductometer model CM20S was used for conductometric measurements at 25°C.

Tetraethylammonium (Et_4N^+) salts were principally used both in mobile phases and as samples to avoid the ion-pair formation in the mobile phases. Lithium nitrate was used as an eluent in MeOH- or H_2O-rich media, where ion-pairs were not formed. Et_4N^+ nitrate and perchlorate were synthesized from Et_4NBr. Tetraethylammonium *p*-nitrobenzoate (Et_4NpNB) and iodide were synthesized from Et_4NOH and a corresponding acid. All Et_4N^+ salts were recrystallized from appropriate solvents. NO_3^- was selected as a primary eluent for three reasons: high solubility in any solvents tested, its moderate absorption below 245 nm, which permitted the detection of transparent anions such as ClO_4^- and Cl^-, and its moderate anion-exchange selectivity. Though it is essential that the same eluent anion is used for all experiments, NO_3^- was not used in DMF, which is not transparent below 270 nm. In solvents containing DMF, pNB^- was used instead of NO_3^-. In all cases, the elution of anions was monitored by an indirect UV mode except for the detection of I^-, pic^-, and SCN^- at 246 nm with NO_3^- eluents because these ions have considerable absorption at this wavelength allowing the appearance of positive peaks. No system peak was observed.

Semiempirical molecular orbital calculation was carried out on a workstation at the Shizuoka University Computer Center. Molecular mechanics calculation was done with a CAChe program based on the MM2 force field on a Macintosh Quadra 650.

3. Results

Figs. 1 and 2 show chromatograms of anions obtained with the combinations of two columns ($-NH_3^+$ and $-NEt_3^+$ polymer matrix resin) with four solvents. Though examples obtained with pure solvents are shown in these figures when possible, the detection of some anions was difficult in some cases because of extremely strong affinity (e.g., Cl^- with the $-NH_3^+$ stationary phase in DMF or MeCN or ClO_4^- with the $-NEt_3^+$ stationary phase in water); for such cases, chromatograms with mixed solvents, containing the solvent of interest as much possible, are shown. Selectivity varies with solvents: $Cl^- < Br^- < I^- < SCN^- < ClO_4^-$ in MeOH and H_2O,

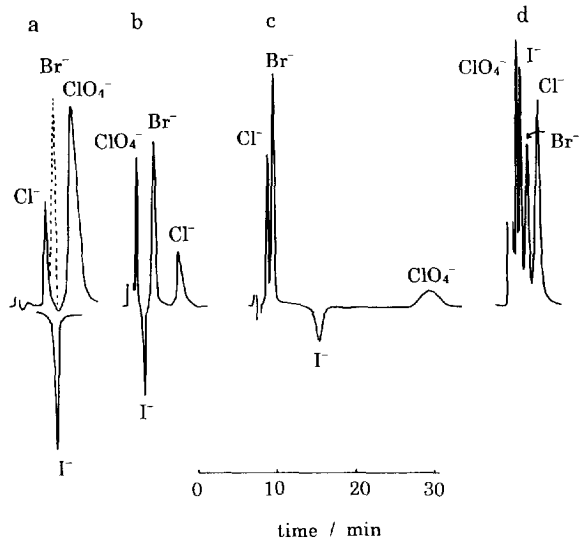

Fig. 1. Anion-exchange chromatograms with the $-NH_3^+$ resin. Mobile phase, (a) 0.02 *M* $LiNO_3$ in MeOH, (b) 0.02 *M* Et_4NNO_3 in MeCN–MeOH (80:20, v/v), (c) 0.02 *M* $LiNO_3$ in H_2O, and (d) 0.01 *M* Et_4NpNB in DMF–MeOH (75:25, v/v). Detection at 246 nm for NO_3^- eluent and at 390 nm for pNB^- eluent. Flow-rate, 1 ml min^{-1} for (a)–(c) and 0.6 ml min^{-1} for (d).

$ClO_4^- < I^-(SCN^-) < SCN^-(I^-) < Br^- < Cl^-$ in MeCN and DMF (in parentheses) irrespective of resin used. We call the former usual (Hofmeister type) selectivity and the latter unusual (anti-Hofmeister type) selectivity. These figures indicate that anion-exchange selectivity can be varied not only by the chemical structure of anion-exchange sites but by the solvent properties.

Fig. 3 shows similar chromatograms obtained with silica-based anion-exchange resins having $Si-NH_3^+$ and $Si\text{-}N(Et)_2Me^+$ anion-exchange sites in MeOH and MeCN–MeOH for comparison. Specific adsorption is thought to be weaker for the silica gel than for the polymer gel. Anion-exchange selectivity is similar except that partially unusual selectivity appears $-NH_3^+$ silica gel even in MeOH. Thus, there is an obvious difference in anion-exchange selectivity between the polymer matrix and the silica gel matrix, suggesting that the specific adsorption on the polymer gel still acts as a part of retention mechanisms even in nonaqueous solvents, although it is much reduced in comparison with in water.

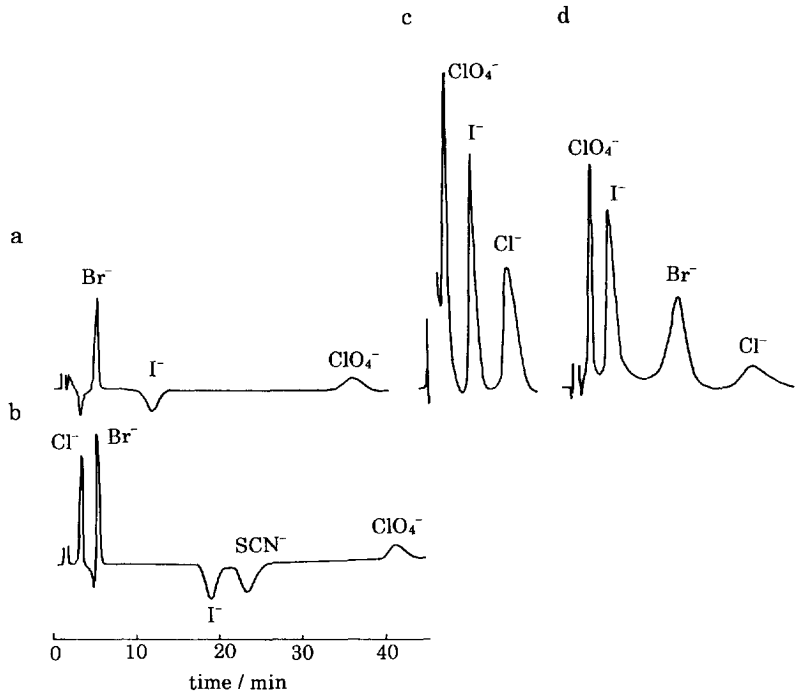

Fig. 2. Anion-exchange chromatograms with the $-NEt_3^+$ resin. Mobile phase, (a) 0.02 *M* $LiNO_3$ in MeOH, (b) 0.01 *M* Et_4NpNB in MeCN, (c) 0.02 *M* $LiNO_3$ in MeCN–H_2O (60:40, v/v), and (d) O.O1 *M* Et_4NpNB in DMF. Detection at 246 nm for NO_3^- eluent and at 395 nm for pNB^- eluent. Flow-rate, 1 ml min^{-1} for (a)–(c) and 0.7 ml min^{-1} for (d).

Figs. 4–7 show changes in the relative capacity factors of anions with compositions of mobile phase solvents. NO_3^- is, in all cases, taken as a reference, and relative k' values (selectivity coefficient) are plotted vs. the volume fraction of mobile phase solvents. Relative k' values are calculated by simply dividing k' of an anion of interest (k_A) by that of NO_3^- (k_{NO3}) for pNB^- eluent and by using the following relation for NO_3^- eluent

$$K_A^{NO_3} = k_A / k_{NO_3}$$

$$= k_A[NO_3^-(m)]/(\phi[NO_3^-(r)])$$

where ϕ is a phase ratio, r and m in parentheses denote resin and mobile phase, respectively. Though it is known that K_A^{NO3} is not constant (in other words, not thermodynamic), this value will be efficient for the description of the selectivity under a condition studied.

4. Discussion

4.1. Comparison of ion-exchange sites

When the differences in selectivity between the $-NH_3^+$ and the $-NEt_3^+$ resin are discussed, the contribution of specific adsorption can be neglected, because the same resin matrix was used for the preparation of both resins. In addition, for MeOH–H_2O–MeCN systems, similar results were obtained with silica gel based anion-exchange resins except that retention of large anions on the polymer anion-exchange resins is slightly larger than that on silica gel based resins in MeOH or H_2O. Thus, in MeOH or H_2O, the specific adsorption contributes to the total retention of large anions to some extent, but is not predominant especially in the absence of water.

The accumulation of solutes in a diffuse double layer will be varied with the surface charge density or ion-exchange capacity [1–3]. As shown in the

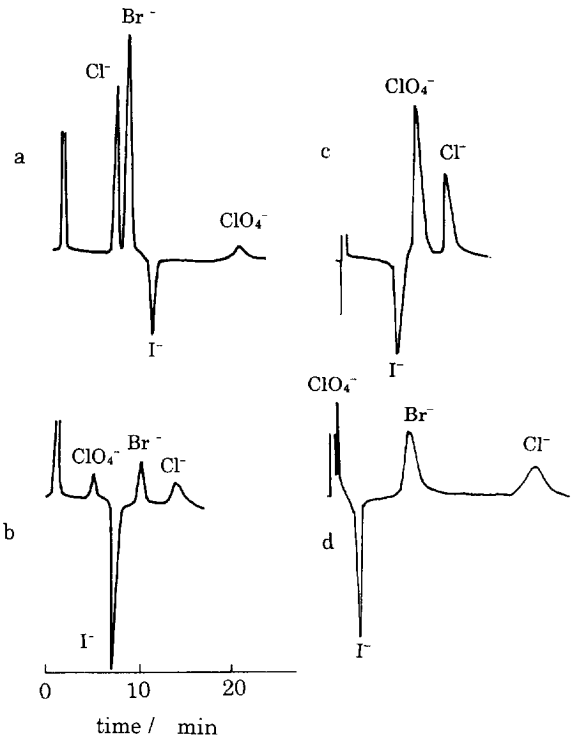

Fig. 3. Anion-exchange chromatograms with silica gel-based anion-exchange resins. Stationary phase, (a,b), TSKgel IC-Anion-SW ($-N(Et)_2Me^+$ anion-exchange resin site); (c,d), amino-propylated silica gel ($-NH_3^+$ anion-exchange resin site). Mobile phase, (a) 0.01 *M* $LiNO_3$ in MeOH, (b) 0.01 *M* Et_4NNO_3 in MeCN–MeOH (75:25, v/v), (c) 0.01 *M* $LiNO_3$ in MeOH, and (d) 0.01 *M* Et_4NNO_3 in MeCN–MeOH (80:20, v/v). Detection at 246 nm.

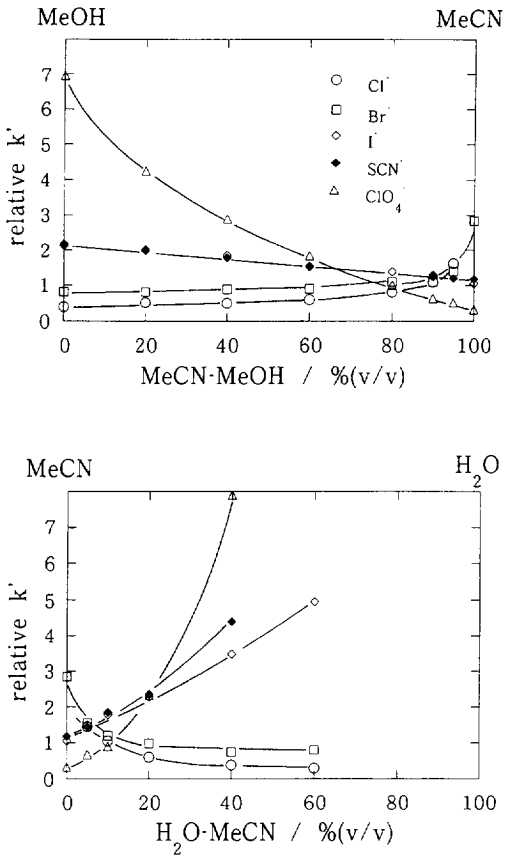

Fig. 4. Changes in relative k' with solvent composition. Stationary phase, $-NEt_3^+$ resin. Mobile phases were containing 0.02 *M* NO_3^- as an eluent; k' values relative to that of NO_3^- were plotted.

experimental section, the ion-exchange capacity of $-NEt_3^+$ resin is slightly smaller than that of $-NH_3^+$ resin. However, this difference is small enough to avoid an essential difference in anion-exchange behaviors. Hence, the difference in anion-exchange selectivity between two resin tested is due predominantly to the specific (hydrogen bond) ion-pair formation and nonspecific interaction between a solute ion and an ion-exchange site. It is known that complete ion-pair formation in an ion-exchange resin should not be necessarily taken into consideration to explain various exchange phenomena. However, all counter ions do exist in the vicinity of the resin surface; e.g., for 0.4 mmol g^{-1} ion-exchange resin, counter ions exist within 2 Å of the resin surface in MeOH according to the calculation based on the electrical double layer model [14]. It is thus reasonable to consider that all counter ions virtually form ion-pairs with ion-exchange sites.

Semiempirical molecular orbital (PM3) calculation with Mulliken charge population analysis indicates that positive charges on a nitrogen atom decrease with increasing number of substituted alkyl groups on the nitrogen atom; e.g., for ethyl substitution, mono-(+0.831)>di-(+0.699)>tri-(+0.592) >tetraethylammonium ion (+0.534), positive charges are given in parentheses. Thus, the $-NH_3^+$ resin has much concentrated charge on the nitrogen atom and is expected to produce the stronger electrostatic field in comparison with the $-NEt_3^+$ resin,

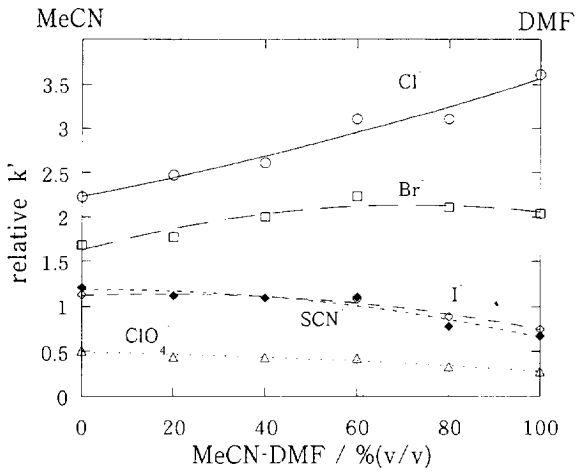

Fig. 5. Changes in relative k' with solvent composition. Stationary phase, $-NEt_3^+$ resin. Mobile phases were containing 0.01 M pNB as an eluent.

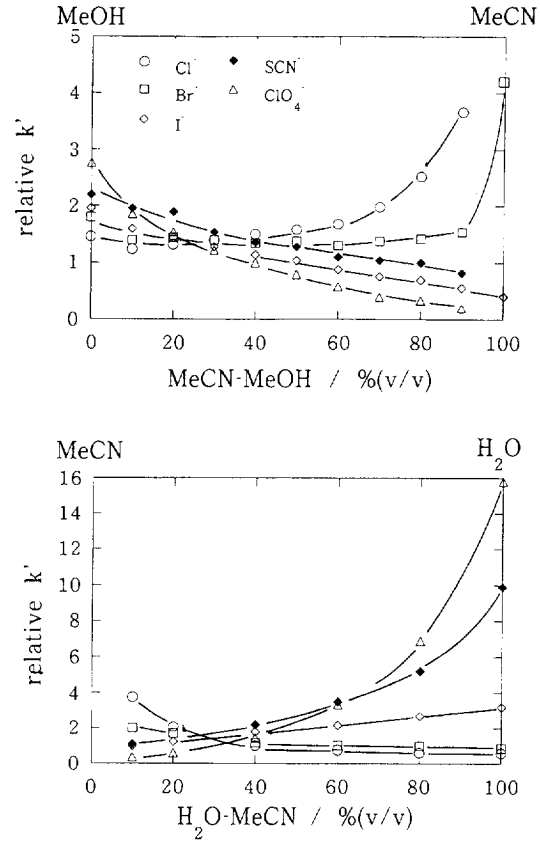

Fig. 6. Changes in relative k' with solvent composition. Stationary phase, $-NH_3^+$ resin. Mobile phases were containing 0.02 M NO_3^- as an eluent.

where a positive charge is dispersed into entire molecules. Electrostatic interaction between an ion-exchange site and a counter ion should occupy a major part of the total mechanism. However, other contributions may not be neglected. Results of a molecular mechanics calculation with the MM2 force field are summarised in Table 2, where two terms, Van der Waals energy (ΔE_{vdw}) and electrostatic energy (ΔE_{el}) including energies of the interaction related to molecular dipole are listed for four combinations of NH_4^+ or NMe_4^+ with Cl^- or I^-. These values are approximate because the calculation based on the MM2 force field is liable to estimate electrostatic energy to be smaller than it should be. However, interesting results are obtained; ΔE_{ele} becomes smaller on going from Cl^- to I^- or from NH_4^+ to NMe_4^+, but ΔE_{vdw} shows opposite trends. The former trend is related to the sizes of ions involved in the interaction, but in contrast the latter trend results from the increasing polarizability of ions. Though ΔE_{ele} is larger than ΔE_{vdw} in all cases, ΔE_{vdw} is not negligible for the interaction between large ions.

For more simple ions, energies contributing to total interaction energy can be calculated. Electrostatic (E_{el}), ion-induced dipole interaction ($E_{i\text{-}id}$), and London dispersion energy (E_{disp}) are thought to be included in total interaction energy. These are calculated for combinations of Cl^- or I^- with Li^+ or Cs^+. Necessary parameters and results of calculation are listed in Table 3 [14,15]. As predicted, E_{el} is largest for LiCl corresponding to the smallest ions combination, but smallest for the largest pair, CsI. In contrast, E_{disp} increases in the order of LiI<LiCl<CsCl<CsI, and CsCl<CsI<LiCl<LiI for $E_{i\text{-}id}$. If ϵ_r is large enough, the contribution of E_{el} determines total interaction energy, and others are negligible. Water, for example, has $\epsilon_r = 78$; if this value were applicable to the present case, $E_{i\text{-}id}$ and E_{disp} would be less than 1% in total interaction energy. However, dielectric saturation near ions will not allow the value the use of bulk dielectric constants [16]; the actual value should be smaller, and the contribution of $E_{i\text{-}id}$ and E_{disp}, becomes more important.

Thus, the change in the chemical structure of

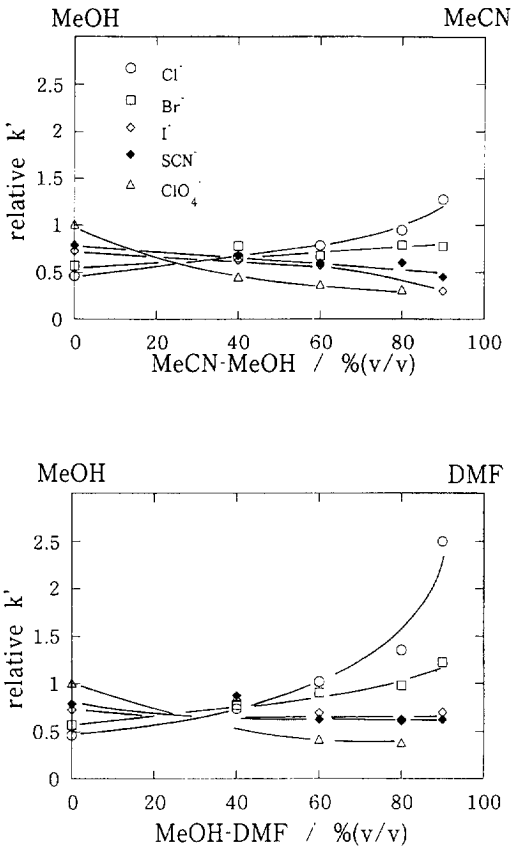

Fig. 7. Changes in relative k' with solvent composition. Stationary phase, $-NH_3^+$ resin. Mobile phases were containing 0.01 M pNB as an eluent.

anion-exchange sites from $-NH_3^+$ to $-NEt_3^+$ principally brings about (1) a decrease in electrostatic interaction due to decreased electrostatic field strength, (2) a decrease in hydrogen-bond formation ability, (3) an increase in ion-induced dipole interaction and London dispersion interaction. Though quantitative evaluation of these three contributions is difficult, all changes are associated with preferable binding of larger ions with the $-NEt_3^+$ resin. Since these are closely related to the extent of solvation, discussion will be focused on this effect in the following section.

Table 2
Electrostatic and Van der Waals interaction energies obtained by MM2 calculation

	ΔE_{vdw}/kJ mol^{-1}	ΔE_{el}/kJ mol^{-1}
NH_4^+–Cl^-	−0.15	−2.81
NH_4^+–I^-	−0.266	−2.586
NMe_4^+–Cl^-	−0.612	−1.863
NMe_4^+–I^-	−0.862	−1.76

4.2. In hydroxylic solvents, MeOH and H_2O

To discuss the actual anion-exchange selectivity, effects of solvation should be taken into consideration; the solvation of ions affects the permittivity for various interactions, interaction distances become short, and interaction energetic gain should partially consumed for desolvation energy.

In MeOH and H_2O, the usual selectivity emerges irrespective of the resin. However, some differences in selectivity are found by detail comparison. Behaviors of ClO_4^- and Cl^- are compared in the following discussion, because these are the most and the least solvated anion tested in the present work and thus the best combination to discuss solvation effects. In MeOH, ClO_4^- is more preferably retained on the $-NEt_3^+$ resin than Cl^- by a factor of 17.4, while the corresponding ratio with $-NH_3^+$, 1.89, is much smaller. The latter value becomes large (27.2) in H_2O, and the former is too large to be measured.

Since the specific ion-pair formation due to hydrogen bond formation is relatively weak in these media, the above difference can be basically explained by ΔE_{el}, $\Delta E_{i\text{-}id}$, and ΔE_{disp}. The $-NH_3^+$ resin has higher charge density, and stronger electrostatic field is produced around this anion-exchange site. Under such a condition, the desolvation of anions will be facilitated upon the binding of a counter anion with an ion-exchange site. If complete desolvation takes place, the smaller Cl^- is more preferably bound to the anion-exchange site than the larger ClO_4^-. In addition, if the desolvation occurs, hydrogen bond formation between an anion and the $-NH_3^+$ site also stabilizes the binding of Cl^-. Though these result in preferable binding of over Cl^- over ClO_4^-, energy should simultaneously be paid for the desolvation process. This energetically unfavorable process results in lower retention of Cl^- than expected only by the electrostatic preference. Though we cannot quantitatively evaluate the extent

Table 3
Calculation of electrostatic (E_{el}), ion-induced dipole ($E_{i\text{-}id}$), and London dispersion energy (E_{disp})

	$r/10^{-10}$ m	$-E_{el}$/kJ mol^{-1}	$-E_{i\text{-}id}$/kJ mol^{-1}	$-E_{disp}$/kJ mol^{-1}
LiCl	2.46	$565/\epsilon_r$	$56.7/\epsilon_r^2$	$0.200/\epsilon_r^2$
CsCl	3.53	$394/\epsilon_r$	$28.2/\epsilon_r^2$	$2.31/\epsilon_r^2$
LiI	2.85	$488/\epsilon_r$	$68.0/\epsilon_r^2$	$0.153/\epsilon_r^2$
CsI	3.85	$361/\epsilon_r$	$30.9/\epsilon_r^2$	$2.58/\epsilon_r^2$

Ionization potential and polarizability for Li^+, Cs^+, Cl^-, and I^- are $I=75.3$, 23.4, 3.61, and 3.06 eV; $\alpha=0.03$, 3.34, 2.96, and $6.43\cdot10^{-30}/(m^3\ (4\pi\epsilon_0))$ respectively. These values are taken from Refs. [14] and [15].

of desolvation by chromatographic experiments, it is reasonable that desolvation is facilitated in the $-NH_3^+$ resin in comparison within the $-NEt_3^+$ resin. In contrast, though the electrostatic stabilization of ClO_4^- by the nonspecific (electrostatic) ion-pair formation is not large, the energy loss for the desolvation process is also small. Thus, the separation window becomes narrow as desolvation is facilitated. As shown in Figs. 1 and 2, the narrower the separation window with the $-NH_3^+$ resin indicates that the desolvation takes place in this resin phase to some extent. This situation is marked for MeOH mobile phases, because desolvation is much easier in MeOH than in H_2O.

In these hydroxylic solvents it is difficult to detect ion-pair formation of 1:1 electrolyte, and therefore only a few data are available in MeOH [17]. According to them, the association constant (K_{IP}) between a tetraalkylammonium ion and a halide ion decreases on going from I^- to Cl^-. This order agrees with an ion-exchange selectivity presented here for the $-NEt_3^+$ resin with MeOH mobile phase. Also, [17] indicates that K_{IP} value becomes small with increasing size of alkyl groups but K_{IP}^{I}/K_{IP}^{Cl} increases. If the interaction other than electrostatic one is dominant, K_{IP} should increase with increasing size of interacting molecules. Thus, this suggests that the interaction between ammonium ions and anions in these hydroxylic solvents is mostly electrostatic and other contribution is marginal.

In water, the specific adsorption becomes more important for the retention of large and less hydrated anions, and thus, such anions are more strongly retained by the resin. This will be reduced in MeOH, but may still acts as an important mechanism to some extent. If the coulombic electrostatic interaction is the only mechanism, the extent of ion-pair formation between a solute and an anion-exchange site can be calculated by Bjerrum or Fuoss equation [9], although these equations do not necessarily give the accurate description for actual ion-pair formation. Ion-pair formation constants vary only by one order of magnitude even when the distance between oppositely charged species is changed from 2 Å to 6 Å. Since difference interaction distances between $M^+-ClO_4^-$ and M^+-Cl^- (M^+ denotes an ammonium ion) will be much less, it will be reasonable that a ratio of electrostatic ion-pair formation constants is much less than 10. However, as shown above, $k'_{ClO_4^-}/k'_{Cl}$ values are much larger than those predicted by theory, suggesting that the contribution of the other mechanism, i.e., the specific adsorption or the change in the water structure in the ion-exchange resin, to entire mechanism is not negligible.

4.3. In aprotic solvents, MeCN and DMF

Anions are poorly solvated in these solvents because of their low acceptor ability, whereas cations are much better solvated in DMF than in MeCN. Judging from the properties of these solvents, differences in donor ability between these solvents will be highlighted in results obtained in these media. Due to the poor solvation ability of MeCN ion-pair formation in solution often takes place in this solvent [18]. Our conductometric measurements (analysis based on the Shedlovski equation [9]) of propylammonium salt, which models the $-NH_3^+$ anion-exchange site, indicated that logarithms of ion-pair formation constants (K_{IP}) are 3.20, 2.17, and 0.70 for Br^-, I^-, and ClO_4^-; that for Cl^- is too large to be evaluated by the Shedlovski equation. In contrast, the ion-pair formation of the tetraethylammonium ion (a model for the $-NEt_3^+$ anion-exchange site) with anions was not detected. K_{IP} values (in parentheses) are reported for

tetramethylammonium (NMe_4^+) chloride (56), bromide (46), and iodide (19) in MeCN, and much smaller for NEt_4^+ salts [17]. It is obvious that hydrogen bond formation is an important factor for governing the ion-pair formation in an aprotic and less basic solvent such as MeCN. These values can be efficient measures for the evaluation of an ion-exchange equilibrium when ion-pair formation due to hydrogen bond formation is a major mechanism.

In MeCN, we encountered the difficulty in the determination of k' for the $-NH_3^+$ resin because of the extremely large k' of Cl^- and small k' of ClO_4^-. We could however detect the peaks of Br^- and I^-; $k'_{Br^-}/k'_{I^-} = 12.2$ which agrees well with the ratio of K_{IP} (10.7) described above. Very low retention of ClO_4^- and extremely high affinity of Cl^- on the resin are also explained principally by specific ion-pair formation; specific ion-pair formation of Cl^- enhances the retention of itself, and that of NO_3^- reduces the retention of ClO_4^-.

For the $-NEt_3^+$ resin, k' of the most retained Cl^- is only 4.2 times as large as that of the least retained ClO_4^-. In this instance, electrostatic interaction will be a major mechanism not including hydrogen bond formation. If the ratio of k' ($k_{Cl^-}/k'_{ClO_4^-} = 4.2$) can be explained by a difference in the distance of electrostatic interaction, this ratio corresponds to a change in the interaction distance, e.g., from 6 Å to 9.8 Å according to the Bjerrum equation though approximate. However, this difference in the interaction distance is still much larger than expected from the size difference between these anions. The comparison of results for halide ions gives clearer results. As stated above, the ion-pair formation constants of these anions with NMe_3^+ in MeCN are known; $K_{IP}^{Cl}/K_{IP}^{Br} = 1.22$ and $K_{IP}^{Cl}/K_{IP}^{I} = 2.95$. The ratios of k' are 1.30 for k'_{Cl}/k'_{Br} and 1.95 for k'_{Cl}/k'_{I}. These values obviously correlates with each other, and thus the ion-exchange selectivity can be explained by electrostatic ion-pair formation observed in solution. However, since ionic radii of these halides are 1.81 Å, 1.95 Å, and 2.16 Å for Cl^-, Br^-, and I^-, respectively [14,15], simple electrostatic interaction or Bjerrum or Fuoss equation cannot quantitatively explain either a K_{IP} ratio or a k' ratio. Hence, for the $-NEt_3^+$ resin, though it is reasonable to conclude that the selectivity in MeCN is determined principally by electrostatic interaction, another factor determining the distance between the cation and an anion may exist.

The situation in DMF is quite similar to that in MeCN as can be seen in Figs. 5 and 7. Ion-pair formation constants of propylammonium salts in DMF are in general smaller than in MeCN because of the strong donor ability of DMF, and increase in the same order as in MeCN, i.e., ClO_4^- (log K_{IP} = 0.80)<I^- (1.11)<Br^-(2.04)<Cl^- (3.00). Unfortunately, these values are not directly compared with k' because we could not determine k' for the $-NH_3^+$ resin in DMF. It is important that anion-exchange selectivity and relative capacity factors obtained in DMF are similar to those MeCN despite the different donor ability. Thus, it appears that the solvation to the cationic anion-exchange sites plays no essential roles in determining anion-exchange selectivity in these aprotic solvents. If we determine the absolute ion-pair formation constant in the resin phase, that in DMF must be smaller than in MeCN as seen for ion-pair formation constants in solution. The fact that the solvation toward cation is not important in the determination of the selectivity agrees with the results of the swelling heat measurements [7], where the swelling heat in different solvents reflects the solvation of counter anions rather than the solvation of cationic anion-exchange resin sites.

Though the anion-exchange selectivity obtained with the $-NEt_3^+$ resin is not changed on going from MeCN to DMF as shown in Fig. 7, a difference in relative retention between a small anion and a large anion is enlarged during this change. This is not associated with specific ion-pair formation in the anion-exchange resin because no ion-pair formation between a tetraalkylammonium ion and an anion was detected in solution, and in addition, changing the solvent leads to no difference in selectivity even for the $-NH_3^+$ resin where specific ion-pair formation plays a decisive role. Thus, the selectivity with the $-NEt_3^+$ resin in DMF is also explained by electrostatic interaction. Tiny differences in relative k' between these solvents will be caused by the smaller acceptor ability of DMF.

A number of investigations have been done for the measurements of swelling behaviors of anion-exchange resin with various solvents and counter anions [7]. According to the results for tetraalkylammonium type resins, Cl^- form anion-exchange resin

swells in water almost five times better than a ClO_4^--form resin of the same crosslinking when compared on the basis of moles of water sorbed in the equivalent resin, whereas the latter swells in DMF almost ten times better than the former. Both results are relevant to the present result. In water, the ion-pair formation between a counter anion and an anion-exchange site is not very strong and the desolvation is not solvated. Under such conditions, Cl^- is solvated much better than ClO_4^-. In DMF, Cl^- is still solvated better than ClO_4^-. However, the strong ion-pair formation takes place in the Cl^- form resin; this reaction is accompanied by the desolvation from both the cation and the anion. In contrast, ClO_4^- forms very weak ion-pairs, and the extent of the desolvation is much smaller.

In conclusion, if the specific adsorption is negligible, anion-exchange selectivity in nonaqueous solvents is determined by the following three factors: (1) the solvation and the extent of desolvation of an anion; (2) specific ion-pair formation between an anion and a cationic anion-exchange site; (3) nonspecific electrostatic interaction. Nonspecific interaction other than electrostatic interaction seems marginal. Though effects of the factor (1) can be predicted from solvent donor and acceptor ability, the donor ability is much less important than the acceptor ability as far as anion-exchange selectivity (relative values) is concerned. The factors (2) and (3) can be evaluated by solution phase ion-pair formation constants, but are not described by simple electrostatic Bjerrum or Fuoss theory. Hence, though we can vary and qualitatively predict anion-exchange selectivity by changing solvent, we must elucidate the solvation of ions in ion-exchange resins for quantitative evaluation of ion-exchange selectivity.

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