Interpretation of chromatographic behavior of ions based on the electric double-layer theory

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Abstract

A retention model based on electrostatic theories is applied to the analysis of the ion-exchange chromatographic separation of ions. The adsorption of counterions and the ion-pair formation between ion-exchange sites and counterions are included in the model; these represent separation selectivity. A nonstoichiometric contribution, the accumulation of ions in an electrical double layer, is also involved in the model. The retention of ions is calculated by assuming these ionic properties for both eluent and solute ions. The comparison of calculated retention factors with experimental values gives insight into the ion-exchange nature of ions; e.g. a strongly adsorbed ion should have higher ion-pair formation ability, and vice versa. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Chromatograms contain useful information on chemistry occurring in a separation column. The shape and width of peaks reflect the kinetic aspects of retention processes as well as their thermodynamics. However, the complexity of chromatographic processes, including not only thermodynamics and kinetics but also hydrodynamics, often makes it difficult to extract the information from peak shapes and peak width [1–3]. In contrast, the mean retention of a sample band should reflect thermodynamic properties of retention mechanisms very well. Therefore, most theoretical researches in chromatography have been conducted to reproduce or predict retention volumes by assuming appropriate equilibria occurring on the stationary phase surface or at the interface between a stationary phase and a mobile phase.

Chromatographic retention is often described by analogy with solvent extraction; a number of successively aligned separation funnels are assumed instead of a separation column. This idea has led to the developments of the plate theory and numerous successes in its applications. However, it should be noted that real stationary phases are heterogeneous, unlike usual organic solvents. Chemically bonded stationary phases, for example, include solid supporting materials and chemically anchored active molecules. The latter should exist in the solution phase rather than in solid-phase. Thus, we cannot assume appropriate two discrete phases in chromatographic separation columns.

This consideration becomes more important in chromatography involving ionic interactions, such as ion-exchange, ion-exclusion, ion-pair chromatography etc. In these chromatographic modes, ionic groups chemically anchored on solid supports should

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exist in mobile phases due to the strong interactions with solvent molecules (solvation). In these cases, we cannot define the boundary between the stationary phase and a mobile phase, and thus should assume successive distribution of mobile phase components from the bulk mobile phase to the surface of the stationary phase [4–7]. The distribution of ionic compounds is affected by electrostatic potential, which is determined by the surface charge density, solution properties, and their charges according to classical electrostatic theories [8–10]. The author has elucidated electrostatic aspects of retention in some chromatographic modes [5–8]. In the present paper, ion-exchange chromatographic separation is discussed on the basis of a previously developed electrostatic ion-exchange chromatographic model [7]. Our attention is paid to the relation between the nature of ions and ion-exchange chromatographic separation selectivity.

2. Experimental

The chromatographic system was composed of a Tosoh computer controlled-pump Model CCPD, a Reodyne injection valve equipped with a 100 μl sample loop, a JASCO UV–visible detector Model 875-UV, and a chart recorder. The separation column, TSKgel IC-Anion-PW, was immersed in water thermostated at 25.0°C. Reagents were of analytical grade. Distilled deionized water was used for solution preparation.

3. Results and discussion

3.1. Retention model

The details of the retention model were previously described [7]. The essential parts of the model are briefly mentioned here. The equilibria taken into account to explain separation selectivity in ion-exchange chromatography are illustrated in Fig. 1; the ion-pair formation between active groups of ion-exchange resins and counterions and the adsorption of counterions. These equilibria can be formulated according to the Boltzmann distribution as follows:
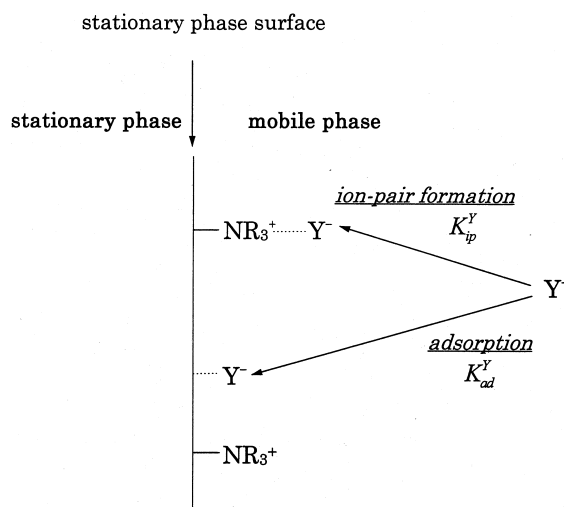

Fig. 1. Schematic representation of retention equilibria.

$$K_{ad}^{X} = \frac{\Gamma_{ad-X}}{\Gamma_{ad}X^0 \exp\left(-\dfrac{z_X F \psi_s}{RT}\right)} \tag{1}$$

$$K_{ad}^{Y} = \frac{\Gamma_{ad-Y}}{\Gamma_{ad}Y^0 \exp\left(-\dfrac{z_Y F \psi_s}{RT}\right)} \tag{2}$$

$$K_{ip}^{X} = \frac{\Gamma_{ie-X}}{\Gamma_{ie}X^0 \exp\left(-\dfrac{z_X F \psi_{st}}{RT}\right)} \tag{3}$$

$$K_{ip}^{Y} = \frac{\Gamma_{ie-Y}}{\Gamma_{ie}Y^0 \exp\left(-\dfrac{z_Y F \psi_{st}}{RT}\right)} \tag{4}$$

where K_{ad}^{X}, K_{ad}^{Y}, K_{ip}^{X}, and K_{ip}^{Y} are the adsorption constants of X and Y, and the ion-pair formation constants of X and Y with active sites, respectively. Γ_{ad} and Γ_{ie} are the surface concentrations of free adsorption sites and free ion-exchange sites. ψ_s and ψ_{st} are the surface and the Stern layer potential. The ion-pair formation occurs at the Stern layer, while the adsorption takes place at the surface; thus, different potentials should be involved in the above equations. In the present paper, X and Y denote an eluent ion and a solute ion, respectively.

There are some reasons that these equilibria are assumed: (1) the adsorption of some ions on ion-

exchange resins is detectable, (2) ion-exchange selectivity can be modified by changing resin matrices, (3) the direct interaction between ion-exchange groups and counterions can be seen in nonaqueous mobile phases [11,12], and (4) ion-exchange selectivity varies with the chemical structures of ion-exchange sites [13,14]; (1) and (2) indicate the importance of the adsorption of ions, while (3) and (4) suggest that ion-pair formation takes an essential part in determining ion-exchange selectivity. Thus, both contributions should be taken into consideration.

The contributions from the adsorption and ion-pair formation of a solute ion to its retention are given by the limiting slopes of adsorption isotherms.

$$k_{ip} = \frac{A}{V_0} \left(\frac{\partial \Gamma_{ie-Y}}{\partial Y^0} \right)_{Y_0=0} \tag{5}$$

$$k_{ad} = \frac{A}{V_0} \left(\frac{\partial \Gamma_{ad-Y}}{\partial Y^0} \right)_{Y_0=0} \tag{6}$$

The contribution from the accumulation of ions in an electrical double layer is given by

$$k_{DL} = \frac{A}{V_0} \int_d^a \left\{ \exp\left(-\frac{z_X F \psi(x)}{RT} \right) - 1 \right\} dx \tag{7}$$

$$\psi(x)$$
$$= \frac{2RT}{F} \ln \left\{ \frac{1 + \tanh(F\psi_{st}/4RT) \exp\{-\kappa(x-d)\}}{1 - \tanh(F\psi_{st}/4RT) \exp\{-\kappa(x-d)\}} \right\}$$

where $1/\kappa$ is the Debye length, $\psi(x)$ is the electrostatic potential as a function of the distance from the charged surface, and d is the thickness of the Stern layer.

Hence, the overall capacity factor is represented by

$$k' = k_{ip} + k_{ad} + k_{DL} \tag{8}$$

3.2. Change in separation selectivity with eluent strength

The ion-exchange chromatographic separation selectivity of several ions was studied by changing eluent strength. The following anions were used both for solutes and for eluents; in the order of increasing anion-exchange selectivity, $IO_3^- < Cl^- < NO_2^- <$ pentanesulfonate $(C5S^-) < Br^- < NO_3^- <$ benzenesulfonate $(BS^-) < I^- <$ toluenesulfonate $(TS^-) <$ octanesulfonate $(C8S^-) < ClO_4^-$. To avoid eluent concentration effects, the retention time of a reference ion was kept constant by adjusting eluent concentrations; unless otherwise stated, NO_3^- was taken as a reference. Although the elution order is not altered by changing eluents, the separation selectivity differs. The results are summarized in Table 1, where the correlation between the relative retention obtained with a Cl^- eluent and that with a different eluent (A) was analyzed by assuming a linear relation as

$$k'_{rel}(A^-) = a + bk'_{rel}(Cl^-)$$

The plots become flat with increasing eluent strength (e.g. 0.910 with $C5S^-$ to 0.521 with ClO_4^-), meaning that the separation becomes worse in this order. No obvious anomalies are found, indicative of the same separation mechanisms as mentioned below.

In order to more clearly show changes in the separation selectivity, the relative retention factors were plotted against the eluent strength as shown in Figs. 2 and 3, where NO_3^- (for Fig. 2) and BS^- (for Fig. 3) were selected as reference anions. The reference retention times were fixed at 12.5 min for NO_3^- and 17.7 min for BS^- by changing eluent concentration. The inverse of the eluent concentration necessary to obtain these appropriate eluent strength was assumed to represent the eluent strength. As anticipated from Table 1, the relative retention factors of strongly retained solutes decrease, while those of weakly retained solutes increase with increasing eluent strength; both seem to

Table 1
Relation between relative retention factors obtained with Cl^- and with a different eluent anion

Eluent	a[a]	b[a]	R[a]
$C5S^-$	0.0608	0.910	0.9985
NO_2^-	0.101	0.885	0.9989
Br^-	0.122	0.868	0.9991
$C8S^-$	0.272	0.697	0.9978
I^-	0.418	0.550	0.9757
ClO_4^-	0.496	0.521	0.9729
$2NS^-$[b]	0.2985	0.8032	0.9885

[a] a = intercept, b = slope, and R = correlation factor based on the linear assumption, $k'_{rel}(A^-) = a + bk'_{rel}(Cl^-)$.
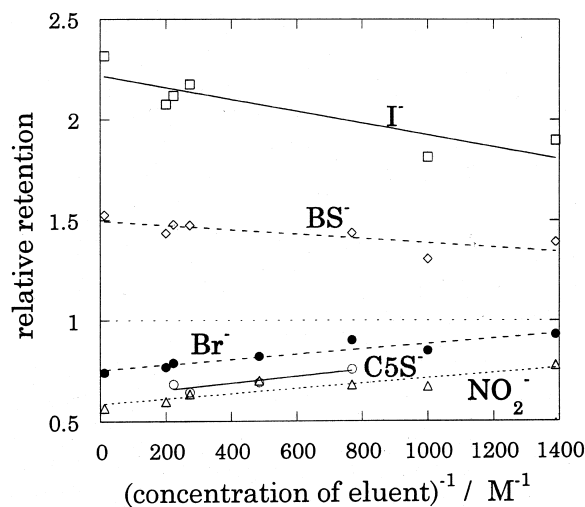
[b] 2-naphthalenesulfonate. NO_3^- was taken as a reference.

Fig. 2. Plots of relative retention factors against inverse eluent concentrations. The retention of NO_3^- was taken as a reference. The eluent concentrations were adjusted to give the retention time of $NO_3^- = 12.5$ min.

approach to unit relative retention at an infinity of strong eluents.

3.3. The adsorption and ion-pair formation ability of an ion
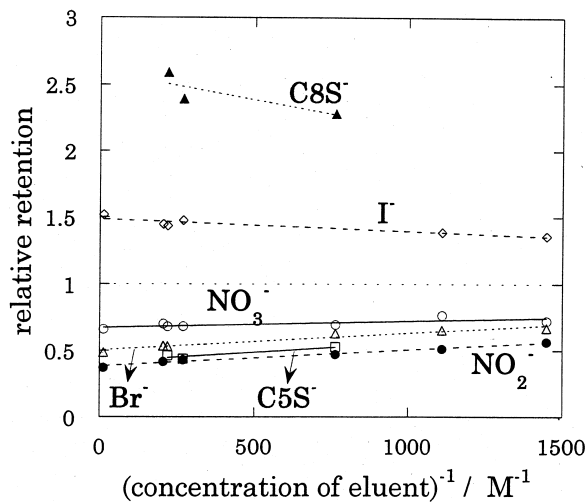
The results shown in Table 1 and Figs. 2 and 3

Fig. 3. Plots of relative retention factors against inverse eluent concentrations. The retention of BS^- was taken as a reference. The eluent concentrations were adjusted to give the retention time of $BS^- = 17.7$ min.
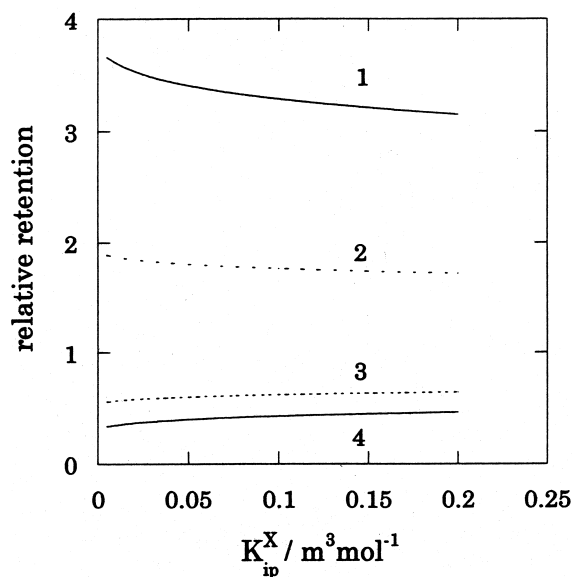

Fig. 4. Calculated plots of relative retention factors against K_{ip}^X. No adsorption was assumed for eluents and solutes. K_{ip}^Y; (1) 0.0125 m^3 mol^{-1}, (2) 0.025 m^3 mol^{-1}, (3) 0.1 m^3 mol^{-1}, (4) 0.2 m^3 mol^{-1}, and 0.05 m^3 mol^{-1} for a reference ion.
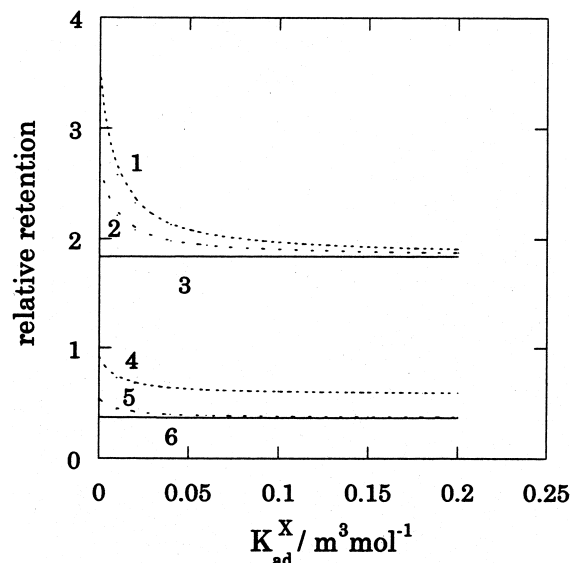

Fig. 5. Calculated plots of relative retention factors against K_{ad}^X. Constant $K_{ip}^X = 0.05$ m^3 mol^{-1} was assumed. (1) $K_{ip}^Y = 0.1$ m^3 mol^{-1} and $K_{ad}^Y = 0.2$ m^3 mol^{-1}, (2) $K_{ip}^Y = 0.1$ m^3 mol^{-1} and $K_{ad}^Y = 0.1$ m^3 mol^{-1}, (3) $K_{ip}^Y = 0.1$ m^3 mol^{-1} and $K_{ad}^Y = 0$ m^3 mol^{-1}, (4) $K_{ip}^Y = 0.0125$ m^3 mol^{-1} and $K_{ad}^Y = 0.04$ m^3 mol^{-1}, (5) $K_{ip}^Y = 0.0125$ m^3 mol^{-1} and $K_{ad}^Y = 0.02$ m^3 mol^{-1}, (6) $K_{ip}^Y = 0.0125$ m^3 mol^{-1} and $K_{ad}^Y = 0$, and $K_{ip}^Y = 0.05$ m^3 mol^{-1} and $K_{ad}^Y = 0$ for a reference ion.

were evaluated by the comparison with the calculation, which is expected to give insights into the solute properties, i.e. adsorptive and ion-pairing abilities. When we calculate the retention of ions according to the above model, the selection of appropriate K_{ad} and K_{ip} values is most important. However, unfortunately, no direct methods are available to determine these constants except for large K_{ad} values. Some typical results of calculations are

shown in Figs. 4–6. Fig. 4 shows changes in relative retention factors with increasing eluent strength, where no adsorption was assumed and thus the eluent strength can be quantitatively represented by K_{ip}^X. The results of calculation are similar to those shown in Figs. 2 and 3; the relative retention factors of strongly retained solutes decreases, while those of weakly retained solutes increases. In contrast, when only the adsorption properties are assumed respon-
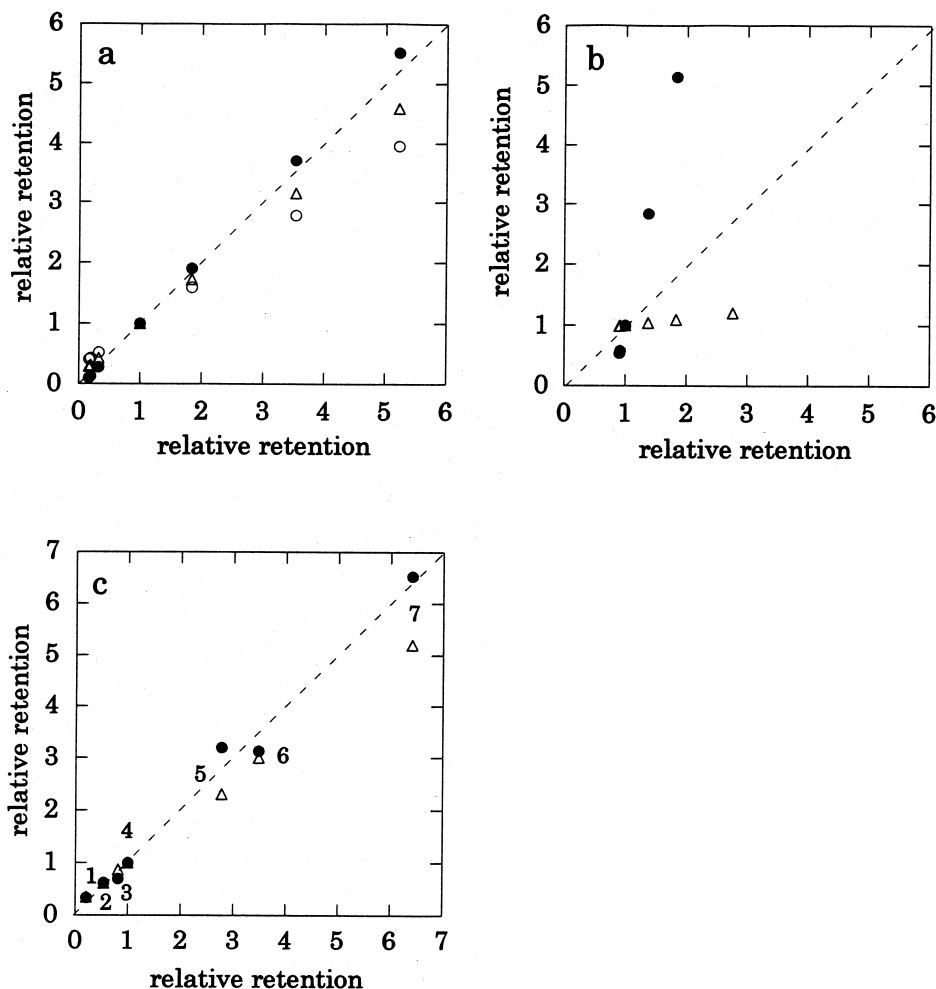

Fig. 6. Correlation between calculated retention factors. (a) No adsorption assumed; $K_{ip}^X = 0.002$ m^3 mol^{-1} for solid circles, $K_{ip}^X = 0.2$ m^3 mol^{-1} for triangles, $K_{ip}^X = 1$ m^3 mol^{-1} for open circles, and $K_{ip}^X = 0.02$ m^3 mol^{-1} for the x-axis; K_{ip}^Y ranged from 0.005 m^3 mol^{-1} to 0.2 m^3 mol^{-1}. (b) Constant ion-pairing assumed; $K_{ip}^X = K_{ip}^Y = 0.1$ m^3 mol^{-1}; $K_{ad}^X = 0.1$ m^3 mol^{-1} for solid circles, $K_{ad}^X = 10$ m^3 mol^{-1} for triangles, and $K_{ad}^X = 1$ m^3 mol^{-1} for the x-axix; K_{ad}^Y ranged from 0 to 20 m^3 mol^{-1}. (c) Both adsorption and ion-pairing varied; $K_{ip}^X = 0.01$ m^3 mol^{-1} and $K_{ad}^X = 0.01$ m^3 mol^{-1} for solid circles, $K_{ip}^X = 0.1$ m^3 mol^{-1} and $K_{ad}^X = 0.01$ m^3 mol^{-1} for triangles, and $K_{ip}^X = 0.01$ m^3 mol^{-1} and $K_{ad}^X = 0$ m^3 mol^{-1} for the x-axis; solute ions (1) $K_{ip}^Y = 0.001$ m^3 mol^{-1} and $K_{ad}^Y = 0$, (2) $K_{ip}^Y = 0.005$ m^3 mol^{-1} and $K_{ad}^Y = 0.02$ m^3 mol^{-1}, (3) $K_{ip}^Y = 0.004$ m^3 mol^{-1} and $K_{ad}^Y = 0.05$ m^3 mol^{-1}, (4) $K_{ip}^Y = 0.01$ m^3 mol^{-1} and $K_{ad}^Y = 0.05$ m^3 mol^{-1}, (5) $K_{ip}^Y = 0.05$ m^3 mol^{-1} and $K_{ad}^Y = 0.1$ m^3 mol^{-1}, (6) $K_{ip}^Y = 0.04$ m^3 mol^{-1} and $K_{ad}^Y = 0.2$ m^3 mol^{-1}, and (7) $K_{ip}^Y = 0.1$ m^3 mol^{-1} and $K_{ad}^Y = 0.3$ m^3 mol^{-1}.

sible for determination of the selectivity (no ion-pair formation), the calculation gives similar but smaller changes for relative retention factors. In the previous paper [7], it was pointed out that the separation is not sensitive to K_{ad} values in the absence of ion-pair formation.

When both ion-pairing and adsorption mechanisms are involved in the model, the relative retention varies in a different manner. In Fig. 5, K_{ip}^X is kept constant and only K_{ad}^Y varies. Seven solute ions including a reference ion ($K_{ip}^Y = 0.05$ m^3 mol^{-1}) were assumed; three of them have larger K_{ip}^Y ($=0.1$ m^3 mol^{-1}), but another three have smaller K_{ip}^Y ($=0.0125$ m^3 mol^{-1}). This means that seven ions give only three peaks if no differences in K_{ad}^Y are assumed. The changes in the relative separation factors are much steeper than those obtained when K_{ip}^Y varies. In addition, the relative retention factors of weakly retained solutes decreases with increasing K_{ad}^X. These do not agree with experimental observations shown in Figs. 2 and 3, suggesting that the ion-pairing mechanism is more realistic than the adsorptive mechanism for present examples.

Plots between relative retention factors obtained with different eluents more clearly show differences between the ion-pair mechanism and the adsorption mechanism. Fig. 6 shows the results of calculation. No adsorption is assumed in Fig. 6a, where the plots are moderately changed, and which agree well with experimental results. In contrast, if constant ion-pairing is assumed, two series of plots depart far from the broken line (unit slope) as shown in Fig. 6b. It should be noted that in both Figs. 6a and 6b the eluent properties were changed by more than two orders of magnitude.

If sulfonate anions had identical ion-pair formation abilities and different adsorption abilities, they should give results similar to shown in Figs. 5 and 6b. However, they behave similarly to other simple inorganic anions. This may imply that the hydration of ions plays a decisive role in determining ion-exchange selectivity because desolvation is generally an important process both for ion-pair formation and for adsorption. In water, it is known that ion-pair formation is an entropy-driven phenomenon because

of very strong solvation ability of water [15]. The hydrophobic interaction, which must be responsible for adsorption in water, is also entropically driven. Thus, it can be a general conclusion that a solute having strong adsorption ability tends to form a strong ion-pair, while weakly adsorbed ions form only weak ion-pairs. If a solute has strong adsorptivity but weak ion-pairing ability, the relative separation factors should give anomalies as shown in Fig. 6c, where two unusual ions are assumed (anomalies can be seen for solutes 3 and 6). However, such clear anomalies cannot be experimentally observed, implying that the above general conclusion is applicable to all ions tested. Thus, the calculation according to the developed theory provides us with information on the ionic nature in water, which cannot be evaluated by chromatographic experiments alone. The present theory and data processing schemes will be useful tools to probe the intrinsic ion-exchange nature of ions.

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