

Review

# Micellar chromatography of inorganic compounds

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## Abstract

Micellar chromatography has been used to separate various compounds and to determine the partition coefficients of the compounds between aqueous bulk solution and a micellar pseudophase. The application of this method to inorganic analyses is less common than its application to organic analyses, albeit the former application gives fundamental aspects of the micellar partition of simple ions and promises developments of novel separation. In this review, we focus our attention on the fundamental aspects of micellar chromatography mostly in inorganic analysis of simple ions. © 1997 Elsevier Science B.V.

*Keywords:* Micellar liquid chromatography; Reviews; Inorganic anions; Inorganic cations

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## 1. Introduction

Molecular aggregates have received much attention as an effective and interesting medium for various reactions and molecular recognition [1–6]; micelles are typical and the most extensively studied representatives. The solution containing micellar aggregates is macroscopically homogeneous, but is

capable of dissolving compounds that are intrinsically insoluble or sparingly soluble in a solvent. This is due to the interaction of solute with micellar aggregates, called micellar solubilization, and is one of the most important and useful features of micelles. Micelles are, e.g., in aqueous solution, composed of a hydrocarbon core, a hydrated hydrophilic (in the cases of ionic micelles, ionic) part, and the interfaces

between solution and a micelle surface, and between a micellar palisade portion and an inner core. This depends on the nature of the micelle and solute as well as on the location of solutes in micelles [7–9].

These properties of micellar solution have led separation scientists to the idea that micelles can be a novel medium for separation [10–26]. Micellar chromatography [10–23] and micellar electrokinetic chromatography [24–26] have for example been developed and extensively employed in various branches of analytical chemistry. Micellar chromatography was initially developed for the separation of organic compounds, and successfully applied to the separation and the determination of partition coefficients of a number of compounds [16–20]. Various micelles, such as anionic, cationic, zwitterionic, nonionic, mixed, and reversed micelles, have been used as chromatographic mobile phases in combination with a variety of stationary phases. However, the application of micellar chromatography to inorganic analyses is not common in comparison with its successful uses in organic analyses. It might be one of the reasons that this method has not given novel selectivity in the framework of usual reversed-phase ion-pair chromatography, and most researchers could not find a practical advantage of this method over ion-exchange or ion-pair chromatography. This is not true as is shown below. If one chooses an appropriate stationary phase, the selectivity can be altered and enhanced even in the separation of inorganic ions. Although the selectivity is determined by the balance between the partition to the stationary phase and that to the micellar phase, reversed-phase micellar chromatography of ionic solutes has mostly been done under the dominant control of retention by the partition to the stationary phase. We could not thus chromatographically detect micellar partition as obvious and dramatic retention changes under such conditions.

On the other hand, the partition of ions to the micellar pseudophase has attracted a number of physical, colloid, and solution chemists, and has often been interpreted with ion-exchange models [27–33]. Such knowledge about the micellar partition of ionic compounds helps us to interpret the micellar chromatographic behaviors of ionic compounds and to design novel separation. The author believes that the opposite is also true; accumulating

chromatographic data is expected to facilitate understanding the micellar chemistry of ionic compounds. In this review, we focus our attention on micellar chromatography of inorganic compounds, mainly ionic inorganic compounds, and will explore the possibility that inorganic micellar chromatography contributes to micellar chemistry and inorganic analyses.

## 2. Partition of ions to ionic micelles

The partition behaviors of ionic species to ionic micellar pseudophases or the specific interaction of ionic species with ionic micelles have been explained by various models often related to the thermodynamics of micellization. It will be significant to briefly touch on this fundamental aspects of micellar formation and micellar partition of ionic species. There are two major thermodynamic theories on micellar formation; a mass action model and a pseudophase model [34,35].

According to a mass action model [36,37], the following equations represent micellar formation, if polydisperse micellar formation is assumed.



where C, S, and M represent a counter ion, a monomer surfactant, and a micelle, and charges are omitted for simplicity. Consideration based on this model and the Gibbs phase theory leads to an important conclusion that a micelle is not a phase but a chemical species. Moroi [36] applied this theory to the determination of a micellar formation constant, the aggregation number of a micelle, and the number of counterions bound by a micelle. Since all equilibrium constants for Eq. (1) could not be determined, monodisperse micelle formation ( $n$  = the aggregation number,  $m$  = the number of counter ions bound by a micelle, and  $K_n$  = micellar formation constant) was assumed.

$$K_n = \frac{\sum_i n_i K_i C^{m_i} S^{n_i}}{n G^m S^n} \quad (2)$$

where brackets representing molar concentrations are omitted. The physicochemical parameters, e.g., for sodium dodecylsulfate (SDS) micelle ( $n=64$ ,  $m=46.7$ , and  $\log K_n=230$ ) were determined on the basis of Eq. (2), indicating that 73% of sodium ions are bound by dodecyl sulfate micelles, but 27% exit as free ions.

According to the Gibbs adsorption equation,

$$d\gamma = -\Gamma d\mu \quad (3)$$

where  $\gamma$ ,  $\Gamma$ , and  $\mu$  are surface tension, a surface excess, and a chemical potential. The surface tension of surfactant solutions decreases with increasing concentration, and becomes almost constant after the concentration exceeds the critical micellar concentration (cmc) of a surfactant. If  $d\gamma=0$  for the concentration of  $>cmc$ ,  $d\mu$  must be equal to zero because  $\Gamma$  is a finite number. This suggests the constant chemical potential of a monomer surfactant in solution, and leads to the idea that micelles can be regarded as a phase because the chemical potentials of monomer surfactants in bulk solution and a micelle should be equal for a phase equilibrium. However, in most cases,  $d\gamma$  is not exactly equal to zero, suggesting that regarding micelles as a phase is an approximate treatment [38–40]. Despite this fact, treating micelles as a phase is very convenient to explain various phenomena taking place in the presence of micelles. As shown later, in micellar chromatography, micelles are mostly treated as a (pseudo)phase. Though this treatment has been employed successfully and has given various valuable knowledge on micellar chemistry, it should be kept in mind that the assumption of a micellar phase is incorrect in a strict thermodynamic sense. Most of ion-exchange models developed to interpret micellar partition of ions are based on this phase separation theory [27–33].

Ion-exchange models in micellar solutions have been applied not only to the interpretation of ionic partition to micelles but also to the explanation of micellar effects on equilibria and kinetics. If the micellar pseudophase is reasonably assumed, an ion-exchange equilibrium can be written as [27]

$$X_{aq} + C_b = X_b + C_{aq} \quad (4)$$

where C and X denote a counterion of micelles and

an ion bearing the same charge as C, respectively, and subscripts aq and b denote an aqueous and a micelle-bound ion. The corresponding selectivity coefficient ( $K^m$ ) can be written as

$$K^m = \frac{X_b C_{aq}}{X_{aq} C_b} \quad (5)$$

In Eq. (5), analytical concentrations are used to define the selectivity coefficient. If the conversion of analytical concentration ( $C_b$ ) to micellar phase concentration ( $C_m$ ) is necessary, it is given by

$$C_m = C_b / (C_M \bar{V}) \quad (6)$$

where  $C_M$  and  $\bar{V}$  represent the micellar concentration and the molar volume of a micelle, respectively. Since the denominator of Eq. (6) is common to X and C, the substitution of micellar phase concentrations in Eq. (6) gives the same selectivity coefficient as defined by Eq. (5).

$C_{aq}$  and  $C_b$  can be written as

$$C_{aq} = \alpha C_M + cmc + C_{add} + X_b \quad (8)$$

$$C_b = (1 - \alpha)C_M - X_b \quad (9)$$

Substitution of Eq. (8) and 9 in Eq. (5) gives

$$K^m = \frac{X_b}{X_{tot} - X_b} \frac{\alpha C_M + cmc + X_b + C_{add}}{(1 - \alpha)C_M - X_b} \quad (10)$$

where  $\alpha$  denotes the degree of counterion dissociation from a micelle,  $X_{tot}$  and  $C_{add}$  are the total concentration of X and the concentration of C added as a salt such as BC. At extremely high micellar concentration, Eq. (10) is reduced to

$$\lim_{M \rightarrow \infty} K^m = \frac{X_b}{X_{tot} - X_b} \frac{\alpha}{1 - \alpha} = \frac{X_b}{X_{aq}} \frac{\alpha}{1 - \alpha} \quad (11)$$

These equations (Eqs. (10) and (11)) allow the calculation of changes in  $X_b$  and  $X_{aq}$  with varying  $C_M$  under various conditions as shown in Fig. 1. Both  $X_b$  and  $X_b/X_{tot}$  increase with increasing  $C_M$  when no salts are added. As predicted by Eq. (11), the latter value converges at  $K^m(1 - \alpha)/\alpha$ ;  $K^m=0.5$  and  $\alpha=0.3$  for the calculation shown in Fig. 1. It can also be seen that increasing  $C_{aq}$  and  $X_{tot}$  causes decrease in  $X_b$  at a given  $C_M$ .

Although  $K^m$  and  $\alpha$  were assumed to be constant

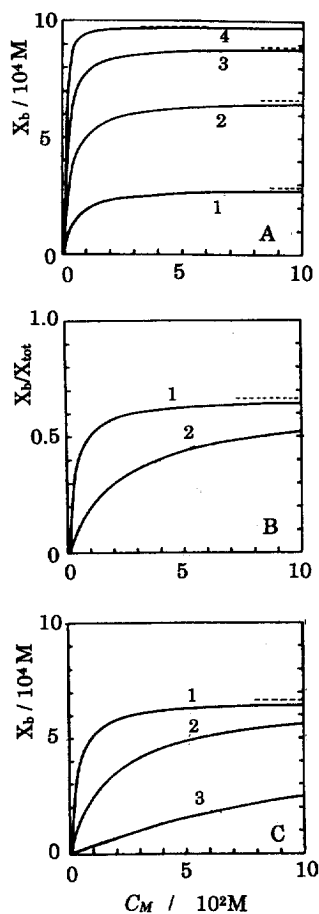


Fig. 1. Calculation based on an ion-exchange model for ion binding of micelles. (A) Dependence of  $X_b$  on  $K^m$  ( $=0.1$  for curve 1,  $0.5$  for curve 2,  $2$  for curve 3, and  $10$  for curve 4)  $X_{tot}=0.1$  mM; (B) Dependence of  $X_b/X_{tot}$  on  $X_{tot}$ ,  $K^m=0.5$ ; (C) Dependence of  $X_b$  on the concentration of an added salt,  $K^m=0.5$ ,  $X_{tot}=1$  mM,  $[BC]=0$  (curve 1),  $0.01$  M (curve 2), and  $0.1$  M (curve 3). Reproduction by the permission of the American Chemical Society from Ref. [27].

in this calculation, it is somewhat questionable to neglect concentration dependencies of these parameters. Although the inconstancy of the ion-exchange selectivity has been well-known [41], treating this as constant has led to a variety of successes in ion-exchange chromatographic studies [42]. Therefore, ion-exchange selectivity is treated as constant throughout this review because this assumption allows derivation of a simple and useful equation. The assumption of constant  $\alpha$  is often employed to

Table 1

Dissociation degree of counter ions of various micelles in the presence and absence of an added salt

Micelles	Conc/M	Salt added	Conc/M	$\alpha$	Ref.
HTAB	— <sup>a</sup>	no		0.16	[48]
		NaCl	0.1	0.10	
HPyC <sup>b</sup>	0.01	NaOH	0.01	0.296	[47]
			0.01	0.271	
			0.01	0.214	
			0.01	0.195	
			0.01	0.170	
			0.006	0.217	
			0.001	0.223	
SDS	0.1	no		0.29	[44]
				0.31	
				0.32	
				0.35	
				0.09	
		NaCl	0.1		[48]

<sup>a</sup> Concentration not specified.

<sup>b</sup> Hexadecylpyridinium chloride.

explain micellar effects on solution equilibria or kinetics, and has allowed the simple derivation of necessary equations or the excellent explanation of various phenomena. However, experimental results have indicated that  $\alpha$  also depends on the concentrations of added salts and surfactant concentration (Table 1) [43–48]. Thus, it must be reasonable that the dissociation of counterions from micelles is represented by a dissociation constant rather than by the degree of dissociation.

### 3. Micellar chromatography of ions

#### 3.1. Comparison of micellar chromatography with ion-exchange and ion-pair chromatography

Ion-exchange chromatography and ion-pair chromatography have been used to separate simple ions, and allowed the accumulation of retention data of ions. Changing the structures of ion-exchange sites or ion-pair reagents and changing mobile phase components have been main topics of this discipline. According to the data obtained from these researches on anion separation (there are a variety of possible structures for anion-exchange sites, usually ammonium ions, while there are fewer possibilities for cation-exchange sites), if large hydrocarbon chains

are introduced on an ammonium nitrogen atom, a larger and less solvated anion is more strongly retained than a smaller and more solvated anion [49–51]. A similar tendency can be seen in usual ion-pair formation taking place in aqueous solution; this can be explained by the hydrophobic interaction where a change in water structures is involved, which is entropically preferable reaction [52]. Basic selectivity in anion separation is often called Hofmeister series, closely related to the hydration states of anions. Although it is known that anti-Hofmeister selectivity can be obtained with a particular stationary phase or with nonaqueous mobile phases, it is in general difficult to alter the selectivity in aqueous chromatography.

In usual ion-exchange and ion-pair chromatography, separation selectivity is given by the stationary phases in the absence of secondary effects; mobile phase additives (typically salts) elute solutes from the stationary phase by mass action, and are less involved in determining selectivity. Fig. 2 shows typical ion-exchange and ion-pair chromatographic separation of some selected inorganic anions, where acid dissociation or complex formation equilibria are not involved in separation and no ion-pair formation in the mobile phase has not been detected, implying that the separation selectivity reflects the interaction of solutes with the stationary phase. Although it is not a main purpose of this review to discuss anion-exchange selectivity, a brief mention of this topic will give a significant insight into the understanding of a role of micellar mobile phases in the separation of inorganic ions because the interaction involved in ionic micellar systems has similar natures to that in ion-exchange.

Although it is difficult to completely explain ion-exchange selectivity, no one doubts that the primary mechanism is electrostatic interaction between an ion-exchange site and a counter ion [53]. Simple electrostatic (Coulombic) interaction is a function of the distance between two charged bodies and the permittivity of a medium. However, this cannot completely explain overall ion-exchange selectivity; ion-exchange selectivity is enlarged in comparison with that predicted by the simple Coulomb theory. A change in interaction distance, e.g., from 0.3 to 0.2 nm corresponds to a decrease in electrostatic energy by  $3 \text{ kJ mol}^{-1}$ ; this results in the enhancement of

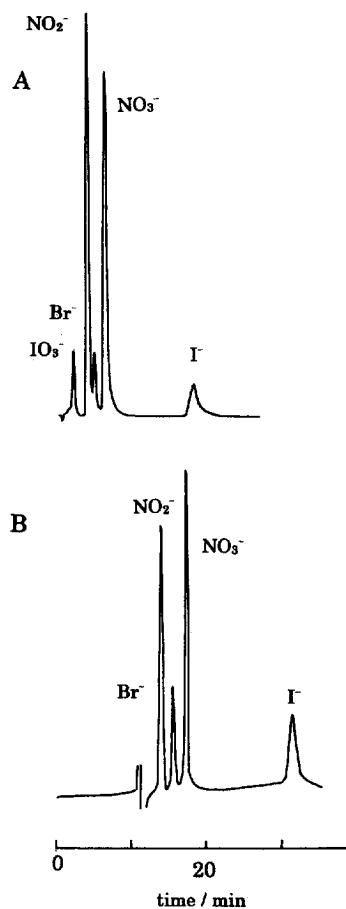


Fig. 2. Ion-exchange (A) and ion-pair (B) chromatographic separation of selected anions. (A) Stationary phase, TSKgel IC-Anion-PW; mobile phase, 20 mM NaCl. (B) Stationary phase, Asahipack GS-310H; mobile phase, 0.05 M tetramethylammonium chloride. Detection, UV at 210 nm (full scale 0.64 AU). Sample concentration, 10 ppm.

retention by ca. 3.5 times, if ion-exchange selectivity is determined only by the electrostatic energy; this seems reasonable. However, a 0.1 nm difference in interaction distance is too large for most of the ions. Although cation-exchange chromatographic separation of  $\text{K}^+$  and  $\text{NH}_4^+$  is not, for example, a very difficult job (e.g.,  $k'_{\text{K}^+}/k'_{\text{NH}_4^+} = 1.20$  [54], 1.28, 1.30 [55], and 1.46 [56]), differences in ionic radius between these two cations are very small, 4 pm in crystalline radii and  $\sim 0$  in Stokes radii [57,58]. This does not necessarily deny the dominant contribution of electrostatic interaction to the overall energetic

origin in ion-exchange selectivity because we do not know exact interaction distances in solution; it is important to take other contributions into account and to describe electrostatic interaction more precisely than usual Coulombic interaction does. Though electrical double layer models have also been proposed, the ion-exchange selectivity has not been successfully explained on a molecular basis [59–63].

Thus, mechanisms other than electrostatic interaction, e.g., solvation (desolvation) of ions, adsorption on the resin matrix, hydrogen bond formation, dispersion force, dipole–dipole interaction, etc., are possibly involved in ion-exchange equilibria [53]. Though the individual contribution from these various mechanisms to overall ion-exchange selectivity cannot be evaluated, it can be empirically deduced that the solvation energies of ions ( $\Delta G_{\text{hydr}}$ ) correlate very well with ion-exchange selectivity [64]. In many cases, there are linear relations between  $\Delta G_{\text{hydr}}$  and  $\log k'$ . As shown later, micellar partition of simple ions can also be related to  $\Delta G_{\text{hydr}}$ .

### 3.2. Chromatographic models

Micellar chromatography has been applied to the determination of partition coefficients of various compounds. The determination of partition coefficients of solutes is based on the following well-known equation [11–13]

$$\frac{V_s}{(V_r - V_0)} = \frac{(P_{\text{MW}} - 1)\bar{V}C_M + 1}{P_{\text{SW}}} \quad (12)$$

where  $V_s$ ,  $V_r$ , and  $V_0$  are the volume of the stationary phase, retention volume of a solute, and the void volume of a separation column, and  $P_{\text{MW}}$  and  $P_{\text{SW}}$  are the partition coefficients of a solute between a micellar and solution (aqueous) phase and between a stationary and solution phase. This equation should hold for ionic solutes as long as two partition coefficients are constant or these coefficients are insensitive to a change in  $C_M$ .

Okada [65] indicated that different equation should be applied to the case where micelles cannot permeate into a particular part of the stationary phase; e.g., micelles are excluded by molecular sieve effects according to their sizes and possibly by electrostatic repulsion [66].

$$\frac{1}{V_r - V_e} = \frac{(P_{\text{MW}} - 1)\bar{V}C_M + 1}{V_i + V_s K_{\text{SW}}} \quad (13)$$

where  $V_i$  and  $V_e$  are the volume of inner solution imbibed by the stationary phase where micelle cannot permeate and that of outer solution where micelles can permeate. This equation is basically the same as Eq. (12) except that solution phase is divided into two parts according to micellar exclusion properties.

It has been verified that micellar chromatographic retention behaviors of simple ions obey Eq. (12); Mullins and Kirkbright [67–70] studied micellar chromatographic retention behaviors of simple anions on usual ODS with cationic surfactants, and Okada explored the applicability of Eqs. (12) and (13) to the description of retention behaviors of anions with cationic [65,71] and mixed micelles [71] and of cations with SDS micelles [72]. In most cases, plots based on these equations were linear, but sometimes gave negative intercepts, which obviously have no physical meaning. There are some possible origins of this problem; (1) it is simply due to experimental error, because direct measurements of retention times are not possible with non-micellar mobile phase, and the intercept is determined by extrapolation; (2) a small change of cmc will result in negative intercepts, because no-one directly determined cmc in chromatographic columns, which is possibly different from the intrinsic value in bulk; (3) it is due to incorrect retention models.

Since the most important interaction between micelles and ions is electrostatic, the mechanism of micellar partition for simple ions must be different from that for electrically neutral organic compounds, which are mostly solubilized in the core or the palisade portion of micelles. Therefore, a retention model characteristic of ionic solutes will better describe their retention behaviors. An ion-exchange model reviewed above is possibly introduced in chromatographic models as discussed below.

### 3.3. Separation of anions

One of the most important and interesting features of micellar chromatography is its unique selectivity. As far as anion separation selectivity is concerned, anti-Hofmeister selectivity is obtained with micellar

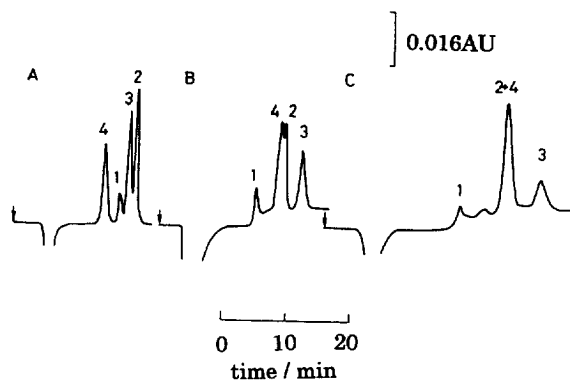


Fig. 3. Comparison of micellar chromatographic selectivity of anion separation. Stationary phases: (A) Asahipack GS-320H, (B) Asahipack GS-310H, and (C) Asahipack GS-300H. These stationary phases are different in the degrees of saponification of polyvinylacetate, and thus have different adsorption ability as shown in Table 2. Mobile phase, (A) and (B) 0.05 M HTAC and (C) 0.013 M HTAC. Peaks: (1)  $\text{IO}_3^-$  (10 ppm), (2)  $\text{NO}_2^-$  (5 ppm), (3)  $\text{NO}_3^-$  (5 ppm), and (4)  $\text{I}^-$  (10 ppm). Detection, UV at 220 nm. Reproduction by the permission of Elsevier from Ref. [71].

mobile phases under particular conditions. Fig. 3 shows examples of anion separation with hexadecyltrimethyl-ammonium chloride (HTMC) as a mobile phase. In usual anion-exchange, the order of anion elution should be  $\text{IO}_3^- < \text{NO}_2^- < \text{Br}^- < \text{NO}_3^- < \text{I}^-$  as shown in Fig. 2, whereas the elution order is partly reversed in the presence of HTAC micelles in mobile phases. It can also be seen that the elution order depends on the nature of the stationary phase. As the adsorption ability of the stationary phase is enhanced (in Fig. 3, the adsorption ability of the stationary phase increases with the order of GS-320H < GS-310H < GS-300H), the selectivity in anion separation approaches to that of usual anion-exchange even with micellar mobile phases. Mullins and Kirkbright [67–70] reported the chromatographic behaviors of anions with hexadecyltrimethylammonium bromide (HTAB) micellar mobile phase, but did not observe a reversed elution order. The dependence of anion separation on the stationary phase natures can be explained by illustrations as shown in Fig. 4, which shows the results of calculation of the retention behaviors of  $\text{NO}_2^-$  and  $\text{NO}_3^-$  with three stationary phases having different adsorption abilities characterized by  $P_{\text{sw}}$  values given in the figure caption. As the adsorption ability of the stationary phase is

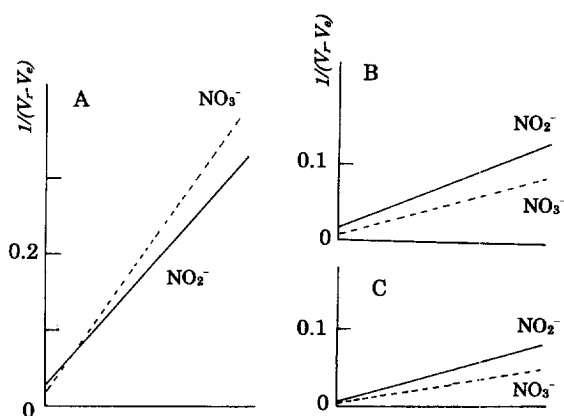


Fig. 4. Relations between  $1/(V_r - V_0)$  for  $\text{NO}_2^-$  and  $\text{NO}_3^-$  and  $C_M$  based on Eq. (13). Stationary phase, (A) Asahipack GS-320H, (B) Asahipack GS-310H, and (C) Asahipack GS-300H.  $P_{\text{sw}}$  values were set to 6.4 for  $\text{NO}_2^-$  and  $\text{NO}_3^-$ .

enhanced, the partition of anions to the stationary phase becomes dominant in determining overall chromatographic separation selectivity. Since the retention in micellar chromatography is determined by a balance between the partition of a solute to the stationary phase and that to the micellar pseudo-phase, if the former predominantly determine the retention, the elution order will be like in anion-exchange or ion-pair chromatography. One may consider that retention order can be reversed with any stationary phases only by increasing micellar concentration. However, as shown in Fig. 4, when the adsorption ability of the stationary phase is higher than a particular threshold, reversed elution order cannot be observed. This is the reason that dramatic changes in elution orders (the intersection of two lines) were not observed with usual reversed-phase chromatographic stationary phases.

Reversed elution order is observed when a salt is incorporated in micellar mobile phases as shown in Fig. 5. Addition of salts induces several effects; i.e., (1) an increase in adsorption amounts of surfactants, (2) a decrease in cmc (or increase in micellar concentration), (3) a change in the micellar shape and aggregation number, and (4) decreases in partition to both stationary and micellar phases by a mass effect. Though salt effects are thus very complex, some effects are negligible or not very important to discuss anion separation selectivity in micellar chro-

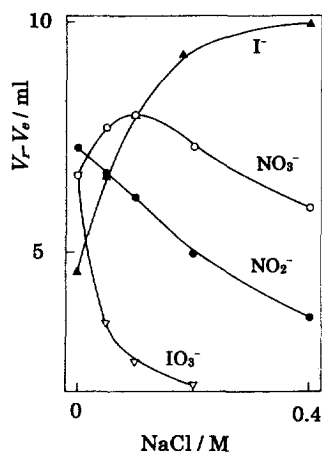


Fig. 5. Effects of adding NaCl to 0.05 M HTAC micellar mobile phase on the retention of some anions. Stationary phase, Asahipack GS-310H 250×7.6 mm). Reproduction by the permission of the American Chemical Society from Ref. [65].

matography. Effect (2) is negligible at least for high surfactant concentration, because 10–200 mM surfactant solutions are usually used as mobile phases and the cmc values of most cationic surfactants range from sub mM to mM. Since there is a simple relation between cmc and added salt concentration(C), such

as  $cmc = a + b \log C$  ( $a$  and  $b$  are constants), the correction of salt effects on cmc is feasible if necessary [73,74]. Effect (3) is also negligible for the micellar partition of simple ions. The electrostatic interaction between an ion and a micellar surface is affected by the surface charge density, which is hardly affected by a micellar shape.

An increase in the adsorption amount of surfactants is important to discuss the retention of ions in micellar chromatography, while this effect may bring about a subtle change in retention of neutral molecules. It is known that an increase in ionic strength results in increasing amount of adsorbed surfactants by a salting-out effect and the diminished repulsion between ionic head groups. Such increases in the adsorption amount of surfactants have been observed in many instances, but depend on the natures of stationary phases as well as those of surfactants as shown in Table 2 [48,71,75]. The increases are not marked for usual reversed-phase stationary phases in comparison with the stationary phase of low adsorption ability, suggesting that surfactant adsorption on the former is almost saturated even in the absence of salts and is not very much enhanced by adding salts.

Table 2  
Adsorption amount of surfactants on various chromatographic stationary phases

Surfactant	Stationary phase	Salt added	Adsorption amount/ $\mu\text{mol m}^{-2}$	Ref.
SDS	SAS Hypersil <sup>a</sup>	no	4.5	[48]
		0.1 M NaCl	4.0	
	ODS Hypersil	no	4.8	
		0.1 M NaCl	5.2	
HTAB	SAS Hypersil	no	4.5	[48]
		0.1 M NaCl	5.5	
	ODS Hypersil	no	4.6	
		0.1 M NaCl	4.6	
HTAC	Asahipack GS-300H <sup>b</sup>	no	0.63	[71]
		no	0.55	
	Asahipack GS-310H	0.1 M NaCl	0.80	
		0.3 M NaCl	1.0	
		no	0.18	
	Asahipack GS-320H	no	0.18	
		0.1 M NaCl	2.2	
Wakosil 5C8 <sup>c</sup>	0.2 M NaCl	2.3		
	0.3 M NaCl	2.2		

<sup>a</sup> SAS Hypersil; trimethylsilyl-modified silica gel.

<sup>b</sup> Asahipack; polyvinylalcohol gel.

<sup>c</sup> Wakosil 5C8; octylsilyl-modified silica gel.

Values from Ref. [48] were read from figures.



These effects are overlapped in the dependence of the retention of anions on salt concentration. In Fig. 5, increases in the retention of  $I^-$  and  $NO_3^-$  (over the low NaCl concentration range) are due to the effect (1) in the above classification. In contrast, decreases in the retention of  $NO_2^-$ ,  $IO_3^-$  and  $NO_3^-$  (over the high NaCl concentration range) are mainly due to the effect (4). Solute anions undergo mass effects to different extents according to the nature of the anions. Judging from marked decrease in the retention of a well-solvated small ion in comparison with that of a large ion, the retention of small ions is dominantly controlled by the partition to the stationary phase, while the micellar partition of large ions dominantly determines their overall retention.

A mass action effect can be quantitatively interpreted by an ion-exchange model [75]. An increase in salt concentration diminishes the partition of anions both to the stationary and to the micellar phase. Taking monovalent anions as examples for simplicity, we need the following two ion-exchange equilibria to describe the retention of anions in micellar chromatography:



where *s* (as both a superscript and a subscript) represents a stationary phase, *A* and *C* are an analyte and a solute anions, charges are omitted for clarity, and  $K^s$  and  $K^m$  denote selectivity coefficients corresponding to equilibria (14) and (15), respectively. Although a selectivity coefficient is not a thermodynamic constant as stated above, treating selectivity coefficients as constants facilitates derivation of a simple equation. It will be reasonable to consider that counter ions in ion-exchange resin are completely bound by ion-exchange sites, while the dissociation of counter ions of micelles should be taken into account. As already mentioned, a dissociation degree ( $\alpha$ ) is often assumed to be constant and independent of the concentrations of surfactants and added salt. A number of data shown in Table 1 indicate that  $\alpha$  is not constant. Therefore, a dissociation constant of counter ions from micelles is assumed:



where  $S - C_m$  and  $S_m$  denote counter ions bound by micelles and a free surfactant molecule binding no counterion in micelles;  $S - C_m$  is introduced to distinguish it from  $S_m$ , but its concentration is the same as  $C_m$  in Eq. (15). The capacity factor of an analyte is given by

$$k' = \frac{\phi A_s}{A_{aq} + A_m \bar{V} C_M} \quad (17)$$

where  $\phi$  denotes the phase ratio. Substitution of equilibrium constants of Eqs. (14)–(17) gives

$$\frac{\phi}{k'} = \frac{C_{aq}}{K^s C_s} \left( 1 + \frac{K^m C_M}{C_{aq} + K_d} \right) \quad (18)$$

This equation indicates that the plot of  $\phi/(k' C_{aq})$  vs  $1/C_{aq}$  will be linear for constant  $C_s$ , if  $K_d < C_{aq}$ , and that we can determine two selectivity coefficients from this relation. Table 3 lists selectivity coefficients determined for selected anions with 0.06 *M* and 0.08 *M* HTAC mobile phases.

Eq. (18) also predicts the dependence of  $k'$  on  $C_M$  in the absence of added salts. If the partition of ions to micelles can be treated in a manner similar to that of neutral compounds, Eqs. (12) and (13) also predict changes in  $k'$  with  $C_M$ . Eqs. (12) and (13) insist the linear changes in  $1/k'$  with  $C_M$ , while Eq. (18) does not necessarily indicate such linear relations because  $C_{aq}$  is a function of  $C_M$ . The calculation and curve fitting based on Eq. (18) indicated that  $P_{MW}$ , which is related to  $K^m$  by Eq. (19), is not constant for ionic compounds, but decreases with increasing  $C_M$ .

Table 3  
Ion-exchange selectivity coefficients for HTAC micelles and the stationary phase adsorbing HTAC [75]

Ion	$C_M = 0.06 \text{ M}$		$C_M = 0.08 \text{ M}$	
	$K^m$	$K^s$	$K^m$	$K^s$
$BrO_3^-$	1.44	1.79	1.37	1.77
$Br^-$	3.09	4.63	2.77	4.32
$I^-$	13.2	33.2	12.1	30.1
$NO_2^-$	1.71	2.05	1.74	2.16
$NO_3^-$	3.55	6.21	3.53	6.17

The stationary phase was Wakosil 5C8. The concentration of NaCl was changed from 0.05 *M* to 0.5 *M* to determine ion-exchange selectivity coefficients on the basis of Eq. (18).

$$P_{\text{MW}} = \frac{K^{\text{m}}}{\bar{V}(C_{\text{aq}} + K_{\text{d}})} \quad (19)$$

This inconstancy of  $P_{\text{MW}}$  becomes negligible with increasing concentration of added salts;  $P_{\text{MW}}$  can be regarded as constant when  $C_{\text{aq}} > 0.05 \text{ M}$ . Table 4 lists  $P_{\text{MW}}$  values for  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , and  $\text{I}^-$  between water and HTAC micelles in the presence of NaCl. These  $P_{\text{MW}}$  values were determined in two different ways; i.e., one is based on Eq. (13), and the other on Eqs. (18) and (19). There are fairly good agreements between two approaches. In particular, the values for small and more hydrated ions agree better than those for large ions. Thus, the micellar partition of ions should be treated by an ion-exchange model rather than by usual pseudophase partition model when mobile phases contain no added salt or the salt concentration is very low. In the presence of added salt of  $>0.05 \text{ M}$ , both approaches give similar results; the simplicity of Eqs. (12) and (13) is advantageous.

There are linear relations between  $P_{\text{MW}}$  or  $K^{\text{m}}$  and  $\Delta G_{\text{hydr}}$  as well as between  $P_{\text{SW}}$  or  $K^{\text{s}}$  and  $\Delta G_{\text{hydr}}$ , suggesting that a basic interaction in micellar chromatography is the same as in usual ion-exchange or ion-pair chromatography despite the difference in overall selectivity.

$$\log K^{\text{m}} (0.06 \text{ M HTAC}) = 5.4 + 0.015 \Delta G_{\text{hydr}} \quad (r=0.974)$$

$$\log K^{\text{s}} (0.06 \text{ M HTAC}) = 7.3 + 0.021 \Delta G_{\text{hydr}} \quad (r=0.982)$$

$$\log P_{\text{MW}} (\text{for HTAC at } 0.2 \text{ M NaCl}) = 8.1 + 0.020 \Delta G_{\text{hydr}} \quad (r=0.956)$$

$$\log P_{\text{SW}} (0.2 \text{ M NaCl}) = 7.3 + 0.021 \Delta G_{\text{hydr}} \quad (r=0.979)$$

Organic solvents are also often used as effective modifiers for micellar mobile phases. It is discussed

from a chromatographic point of view that addition of a small amount of organic solvents improves peak shapes because of the reduced interfacial resistance for the mass transfer due to better wetting of the reversed-phase surfaces, and the enhancement of the separation selectivity has been reported [18,76]. However, in micellar chromatography of inorganic ions, the addition of organic solvents results in simple decreases in retention [65,67,68]. The quantitative interpretation of retention data is difficult under such conditions because the coexistence of organic solvents disturbs the micellization, and changes the shape and the properties of micelles. More studies on micelle-organic solvent mixtures are necessary to facilitate to understand the partition behaviors and the chromatographic retention of ions in such mixed micellar phases; for this purpose, cooperative uses of chromatography with other methods are also important [77,78].

The applicability to complex matrices has been pointed out as one of advantages of micellar mobile phases; e.g., biological samples contain proteins and other polymeric compounds, which are deposited in usual hydro-organic mobile phases and cause problems. From such a viewpoint, micellar chromatography has been recently applied to the analyses of some environmentally important inorganic compounds, such as arsenic species, in combination with ICP-MS detection. Micellar mobile phases containing HTMB showed good compatibility with the detection method, and were successfully employed to separate As(III), As(V), monomethylarsonic acid, and dimethylarsonic acid [79]. Further utilization of micellar chromatography in such applications is expected.

### 3.4. Separation of metal species

The basic treatment of the retention behaviors of cations in micellar chromatography is the same as for the separation of anions. It is usually difficult to chromatographically separate various cations having the identical charge and similar hydration energies, e.g., divalent transition metal ions, with simple salt solution as a mobile phase. Various ligands are therefore incorporated in mobile phases to enhance the ion-exchange separation selectivity in such cases; for the separation of divalent transition metal ions,

Table 4  
 $P_{\text{MW}}$  determined by a pseudophase model (Eq. (13)) and an ion-exchange model (Eqs. (18) and (19)) [71,75]

	$P_{\text{MW}}$					
	Pseudophase			Ion-exchange		
	$\text{NO}_2^-$	$\text{NO}_3^-$	$\text{I}^-$	$\text{NO}_2^-$	$\text{NO}_3^-$	$\text{I}^-$
0.1 M NaCl	37.8	100	615	46.7	93.4	357
0.2 M NaCl	23.6	56.6	341	23.4	46.7	179
0.3 M NaCl	16.2	43.1	226	15.6	31.1	119

tartaric acid, citric acid, etc., are often employed [80]. In micellar chromatography, addition of such ligands results in the complicated interpretation of the retention data, because complex formation equilibria should be taken into consideration in addition to ion-exchange equilibria or micellar pseudophase partition. Since neutral and anionic species are possibly formed as a result of complexation, the partition these species should be taken into consideration if necessary; (in most cases, the partition of hydrophilic neutral species and species having the same charge as micelles is negligible). As stated above, Eq. (12) and Eq. (13) instead of Eq. (18) are applicable to mobile phases of sufficiently high ionic strength. In such cases where we should consider complex formation of analyte cations, it will be convenient to investigate the natures of apparent partition coefficients rather than to study the changes in retention times. Detailed studies were conducted on the partition coefficients of divalent transition metal ions to SDS micelles in the presence of tartaric acid as a ligand [81]. Tartaric acid forms complexes with divalent transition metal ions ( $M^{2+}$ ) as typically shown by the following equilibria.



where  $L^{2-}$  and  $HL^-$  are divalent and monovalent tartrate species. In most cases, it is not necessary to take multiple complex formation such as  $ML_2^{2-}$  into consideration. The apparent partition coefficients determined according to Eq. (12) or Eq. (13) can be written as [81]

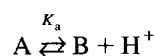
$$P_{MW}^{app} = \frac{[M^{2+}]_m}{[M^{2+}]_{aq} + \beta_{HL}[M^{2+}]_{aq}[HL^-] + \beta_L[M^{2+}]_{aq}[L^{2-}]} \quad (22)$$

Assuming a single counter ion, in this case  $Na^+$ , Eq. (22) can be rewritten by substituting equilibrium constants in Eq. (22) as

$$\frac{1}{P_{MW}^{app}[Na^+]_{aq}^2} = \frac{1 + (\beta_{HL}[H^+]/K_2 + \beta_L)[L^{2-}]}{K^m[Na^+]_m^2} \quad (23)$$

where  $K_2$  is the second dissociation constant of tartaric acid. A similar equation should hold for  $P_{SW}^{app}$  by changing  $K_m$  by  $K_s$  and  $[Na^+]_m$  by  $[Na^+]_s$ . Eq. (23) indicates that there is a linear relation between  $1/(P_{MW}^{app}[Na^+]_{aq}^2)$  and  $[L^{2-}]$ . Such linear relations were confirmed for  $P_{SW}^{app}$ , but not for  $P_{MW}^{app}$ . For  $P_{MW}^{app}$ , linear relations between  $1/P_{MW}^{app}$  and  $[Na^+]_{aq}^2$  rather than between  $1/(P_{MW}^{app}[Na^+]_{aq}^2)$  and  $[L^{2-}]$  were obtained, albeit there was a discrepancy that the lines do not pass the origin probably because constant  $[Na^+]_m$  was assumed [81]. These facts clearly indicate that tartaric acid acts as an effective ligand in the partition of transition metal ions to the stationary phase, but does not act as a ligand at all in the partition to the micellar pseudophase. This is due to the shift of the dissociation equilibrium of tartaric acid in the presence of micelles (by the negative surface potential of SDS micelles).

There are a number of data showing micellar effects on acid–base equilibria [82–86]. Shifts of an acid–base equilibrium in the presence of micelles have been explained in two ways. One is based on an ion-exchange model, where the partition of neutral species of an acid to the micellar pseudophase and ion-exchange equilibria for a counterion, for foreign ions, and for hydrogen ion (and/or hydroxide ion) are taken into consideration [27]. The other is a more common model based on an electrostatic model derived from the Boltzman equation. Fernández and Fromherz [82] distinguished the following three typical cases for the acid–base equilibrium occurring at the interface between solution and membrane (or micellar) phase: (1) a membrane-bound acid is dissociated into a membrane-bound base and a hydrogen ion in bulk solution; (2) a membrane-bound acid is dissociated into a membrane-bound base and a hydrogen ion in solution near membrane; (3) a membrane-bound acid is dissociated into a membrane-bound base and a membrane-bound hydrogen ion (similar to the equilibrium in nonaqueous solutions). In all cases, both an acidic and a basic form of an indicator compound were assumed to be bound by the membrane. In bulk water, the acid dissociation constant of an indicator is represented by



$$pK_a = \frac{\mu_{H^+}^{\circ w} + \mu_B^{\circ w} - \mu_A^{\circ w}}{2.303RT} \quad (24)$$

where  $\mu_i^{\circ w}$  denotes the standard chemical potential of species *i* in bulk water. When a micelle-bound acid is dissociated into a micelle-bound base and a hydrogen ion in water (case 1 in the above category), the acid dissociation constant ( $K^{MW}$ ) is given by

$$pK_a^{MW} = \frac{\mu_{H^+}^{\circ w} + \mu_B^{\circ m} - \mu_A^{\circ m} - F\psi}{2.303RT} \quad (25)$$

where  $\mu_i^{\circ m}$  is the standard chemical potential of species *i* in a micellar phase and refers to the surface potential of a micelle. Micellar effects on  $pK_a$  is given by

$$\Delta pK^{MW} = pK_a^{MW} - pK_a = \Delta pK^i - \frac{F\psi}{2.303RT} \quad (26)$$

$$\Delta pK^i = \frac{(\mu_B^{\circ m} - \mu_B^{\circ w}) - (\mu_A^{\circ m} - \mu_A^{\circ w})}{2.303RT}$$

The first term on the right side of Eq. (26) shows a medium effect and the second term does a surface potential effect. The surface potential of micelles have been determined using various micelle-bound indicator according to Eq. (26); e.g.,  $\Psi = \text{ca. } -100$  mV for SDS micelles [82]. The  $pK_a$  of tartaric acid at the SDS micelle–water interface cannot be determined with above assumptions because any species of tartaric acid will more stably exist in bulk water rather than in micellar phases. However, it is expectable that  $pK_a$  in a micellar phase will be much larger than  $pK_a$  in bulk water because the concentration of  $H^+$  is higher than in bulk water whereas those of tartrate ions will be lower than in bulk water due to the negative surface potential of SDS. This discussion implies that the dissociation of tartaric acid is reduced at the SDS–water interface due to the negative surface potential of SDS, and that the complex formation of metal ions with tartrate is also suppressed as a result. Though the similar should be thought to be true for the stationary phase surface [87], it is reasonably predicted that the surface potential of the stationary phase is numerically much lower than that of SDS because of lower surface charge density of the stationary phase surface. Thus, the effect of the surface potential of the stationary

phase on the complex formation is too weak to be chromatographically detected.

In micellar chromatography, it has been debated whether micellar mobile phase enhances the separation performance or not [76]. Since, in particular, similar separation of transition metal ions is possible with non-micellar mobile phase, it should be clarified whether use of micellar mobile phases improves resolution or enhances separation factors. We can simulate the separation with very simple linear relations represented by Eq. (23); changeable experimental parameters are the concentration of SDS, pH, and the concentration of tartaric acid. Thus, the simulation of, e.g., minimum separation ratios is possible in a three dimensional space comprised of these three parameters. Fig. 6 shows two-dimensional cross-sectional contour maps, where the separation of six transition metal ions (Mn(II), Co(II), Cd(II), Zn(II), Ni(II), and Pb(II)) was studied by calculating minimum separation ratios. It is obvious that the presence of micelles improved the separation in comparison with the absence of micelles in the

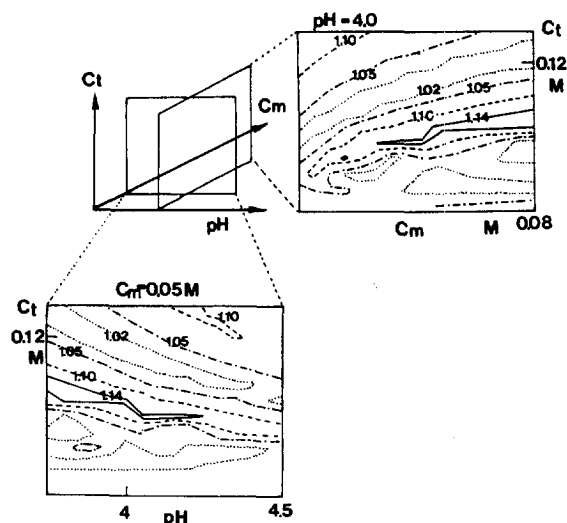


Fig. 6. Contour plots of calculated minimum separation ratios obtained at the different cross-sections of the three-dimensional representation composed of the concentration of tartaric acid ( $C_t$ ),  $C_m$ , and pH. Separation was studied for six transition metal ions, Cd(II), Co(II), Mn(II), Ni(II), Pb(II), and Zn(II), and thus the minimum separation ratio was selected from possible 15 combinations. Stationary phase, Inertsil ODS (150 mm  $\times$  4.6 mm I.D.). Reproduction by the permission of the American Chemical Society from Ref. [81].

mobile phases. Results of simplex optimization indicated that there are some local maxima for minimum separation ratios in this three-dimensional space, but mobile phases containing micelles always gave better results than non-micellar mobile phases. Fig. 7 shows a chromatogram obtained under an optimized condition.

Separation of lanthanoid ions has usually been done by ion-exchange chromatography with mobile phases containing  $\alpha$ -hydroxyisobutyric acid ( $\alpha$ HB) or lactic acid. SDS micellar mobile phases containing these ligands have also been studied for this purpose [88,89]. If a sample contains lanthanoid ions but no other metal ions, gradient elution is useful because their properties change stepwise with their atomic numbers, and thus the optimization scheme for the separation is relatively simple in this separation. Coexistence of other transition metal ions in a sample however makes the optimization of separation difficult and complicated. Complete description of ion-exchange process at solution/ion-exchange resin and at solution/micelle interface is very complex because one-three monovalent ligand molecules possibly coordinate lanthanide ions. For simplicity, it was assumed that only  $M^{3+}$  species can be

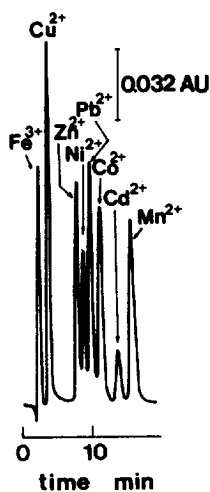


Fig. 7. Chromatogram obtained under the condition optimized by a simplex method in the three-dimensional space shown in Fig. 6. Mobile phase, 0.0945 M SDS + 0.0684 M tartaric acid (pH = 4.02). Sample concentration, 0.25 mM Fe(III), 0.4 mM Cd(II) and Zn(II), 0.05 mM Cu(II) and Mn(II), and 0.02 mM Co(II) and Ni(II). Stationary same as Fig. 6. Reproduction by the permission of the American Chemical Society from Ref. [81].

partitioned to ion-exchange resin and to micellar phase but that partitioning of other divalent and monovalent species is negligible. According to this assumption,  $k'$  of a lanthanide ion is given by [88]

$$k' = \frac{\phi[M]_s}{[M]_{aq} + \sum[ML_i] + [M]_m \bar{V}C_M} \quad (27)$$

where  $ML_i$  denotes 1: $i$  complex of a metal ion with  $\alpha$ HB. Substituting necessary equilibrium constants in Eq. (24) gives

$$\phi/k' = B_1 + B_2[L]^n \sum D_i [L]^{3+i} \quad (28)$$

$$B_1 = \bar{V}M[Na]_m^3 / K^m$$

$$B_2 = 1/[Na]_s^3 K^s$$

$$D_i = \frac{\sum \beta_i [L]^i}{[Na]_s^3 K^s}$$

where  $\beta_i$  denotes an overall formation constant of 1: $i$  complex, and  $[L] = [Na]$  can be reasonably assumed. Table 5 lists these parameters for lanthanoid ions and other divalent transition metal ions, indicating that 1:3 complexes are formed for lanthanoid ions, a 1:2 complex is formed for Cu(II), and no complexes are formed for other divalent cations listed. Though these values should have physicochemical meanings shown in Eq. (28),  $\beta_i$  values, calculated from  $D_i$  and  $B_2$ , are much smaller than values tabulated in the literature [90]. This must be due to the effect of negative surface potential of the stationary phase adsorbing SDS, but has not been quantitatively evaluated.

In chromatography of metal species, separation of more inert complexes (or metal chelates) is also important. Reports on micellar chromatographic separation of chelates are not as many as those on chromatography with usual hydro-organic solvents [91–94]. Interpretation of micellar chromatographic behaviors of metal chelates is difficult because the various interactions other than electrostatic should be simultaneously considered due to their more hydrophobic natures. It is expected that a number of data of micellar partitioning in solvent extraction and related work facilitate to develop novel application of micellar chromatography to this chemistry.

Table 5  
List of parameters for transition metal ions based on Eq. (30) in Ref. [88]

Metal ion	$B_1$	$B_2$	$D_1$	$D_2$	$D_3$
Yb(III)	0.026	$6.72 \cdot 10^3$	$4.66 \cdot 10^4$	$3.05 \cdot 10^5$	$4.60 \cdot 10^6$
Tm(III)	0.030	$4.90 \cdot 10^3$	0	$3.30 \cdot 10^5$	$4.30 \cdot 10^6$
Er(III)	0.030	$3.50 \cdot 10^3$	0	$3.00 \cdot 10^5$	$3.00 \cdot 10^6$
Ho(III)	0.030	$1.65 \cdot 10^3$	0	$2.41 \cdot 10^5$	$2.81 \cdot 10^6$
Dy(III)	0.031	899	0	$2.27 \cdot 10^5$	$2.81 \cdot 10^6$
Tb(III)	0.025	670	0	$8.70 \cdot 10^4$	$1.04 \cdot 10^6$
Gd(III)	0.024	260	5.3	$5.97 \cdot 10^4$	$7.46 \cdot 10^5$
Eu(III)	0.023	160	43.6	$5.07 \cdot 10^4$	$5.65 \cdot 10^5$
Sm(III)	0.021	140	1.29	$2.65 \cdot 10^4$	$4.54 \cdot 10^5$
Cu(II)	0.23	0.042	0.82	$3.27 \cdot 10^4$	
Zn(II)	0.068	26.5	0	0	
Ni(II)	0.073	19.6	0	0	
Co(II)	0.077	12.3	0	0	
Mn(II)	0.077	6.24	0	0	
Cd(II)	0.069	6.27	0	0	

Determined with 0.1 M SDS containing 0.02–0.08 M [L] ( $L = \alpha\text{HB}$ ) on Inertsil ODS2.

#### 4. Simultaneous separation of solutes of different classes

Micellar mobile phases allow various simultaneous separations, which is difficult or impossible with nonmicellar mobile phases. The simultaneous separation of phenols and various inorganic ions has been carried out with micellar mobile phases as an application of the above mentioned ionic separation [88,95]. Separation of neutral organic compounds such as phenols can be controlled by changing the concentration of micelles but is insensitive to changes in salt concentration. On the other hand, the retention of ionic compounds can be determined not only by the concentration of micelles but by the concentration of ionic additives, the concentration of ligand, pH, etc. Since it is difficult to simultaneously fulfil the conditions required by several different analyses, a more simple scheme was proposed [88]. The micellar concentration is optimized for the separation of neutral compounds first and then other conditions are optimized if separate detection is possible, e.g., for the separation of phenols and transition metal ions with SDS mobile phases, where the former is detectable with the usual UV detection and the latter with postcolumn reaction with an appropriate reagent. If a single detection method should be used, e.g., for the separation of phenols

and UV-absorbing anions, simultaneous optimization of the mobile phase composition is necessary.

Fig. 8 shows an example of separation of phenols and transition metal ions, while Fig. 9 shows that of phenols and anions. For the former analysis, phenols were detected by the usual UV absorption and then transition metal ions were detected by postcolumn reaction with PAR. The concentration of SDS was first optimized for the separation of phenols, and then the separation of metal ions was optimized on the basis of Eq. (28). In contrast, since both phenols and anions were detected with a UV detector, the optimization was done by a simplex method on the  $C_M - C_{aq}$  surface of minimum separation factors, where the retention of phenols was expected by Eq. (12) and that of anions by modified Eq. (18) [88]. Though the optimization procedure is complicated and needs various experimental parameters, simultaneous separation of compounds of different intrinsic natures is one of the versatile features of micellar chromatography.

Hu and Haraguchi [96–102] have showed another approach to simultaneous separation, where zwitterionic micelles were utilized. Adsorption equilibria of ionic surfactants are usually established between monomer surfactants in solution and adsorbed surfactants; adsorbed amounts become constant after the concentration of surfactants reaches the cmc. How-

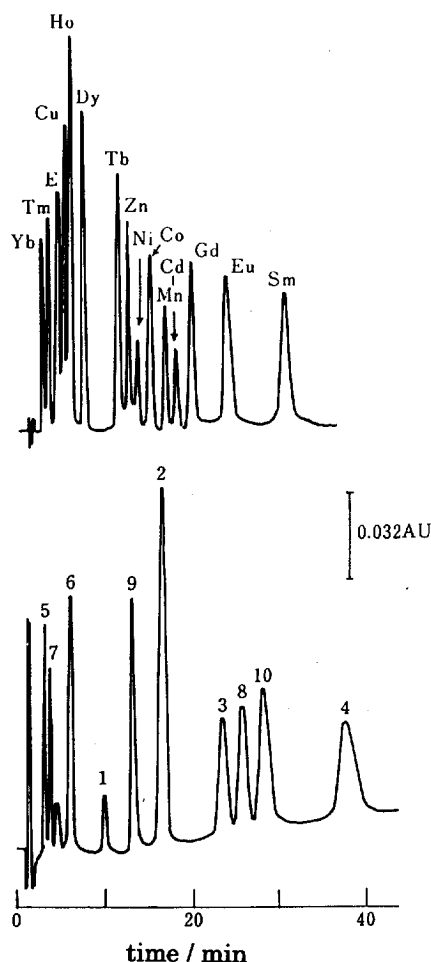


Fig. 8. Simultaneous separation of phenols and metal ions with SDS micellar chromatography. Phenols were detected with UV detection at 280 nm. Metal ions were detected at 540 nm after the postcolumn reaction with PAR. Stationary phase, Inertsil ODS-2 (150 mm×4.6 mm I.D.). Mobile phase, 0.1 M SDS and 0.08 M  $\alpha$ HB (pH=4.05). Peaks for phenols: 1, phenol; 2, *p*-cresol; 3, *p*-ethylphenol; 4, *p*-*tert*-butylphenol; 5, *p*-hydroxybenzylalcohol; 6, *p*-hydroxybenzaldehyde; 7, resorcinol; 8, *p*-chlorophenol; 9, *p*-nitrophenol; 10, 1-naphthol. Reproduction by the permission of the Japan Society for Analytical Chemistry from Ref. [88].

ever, in some cases, adsorption amounts continue to increase after the surfactant concentration in solution phase increases beyond cmc; multilayer adsorption or micellar sorption possibly take place. Hu and Haraguchi treated their data assuming the interaction of micelles adsorbed on ODS stationary phases with

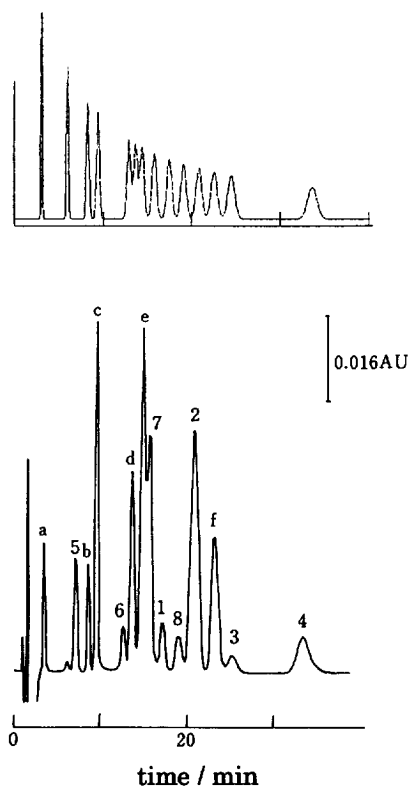


Fig. 9. Predicted (upper) and experimentally obtained chromatograms of a mixture of phenols and inorganic anions. Stationary phase, the same as for Fig. 10. Mobile phase, 0.068 M HTAC and 0.049 M NaCl. Peaks for phenols (numerically labeled) given in Fig. 9. Peaks for anions: a,  $\text{IO}_3^-$ ; b,  $\text{BrO}_3^-$ ; c,  $\text{NO}_2^-$ ; d,  $\text{Br}^-$ ; e,  $\text{NO}_3^-$ ; f,  $\text{I}^-$ . Reproduction by the permission of the Japan Society for Analytical Chemistry from Ref. [88].

ionic solutes; no detail adsorption data have been reported, and thus it is difficult to confirm this interaction from published data. Though micellar mobile phases were not used in a series of their work, this work belongs to a modified micellar chromatography if adsorbed surfactants act as micelles. Fig. 10 shows a typical separation with ODS adsorbing 3-[(3-cholamidopropyl) dimethylammonio]-1-propanesulphonate (CHAPS) bearing both tetraalkylammonium cation and sulfonate anion in its molecule. This stationary phase acts both as cation and as anion-exchanger, and is capable of separating both anions and cations. Interestingly, solutes are eluted by all possible combinations; e.g., when a

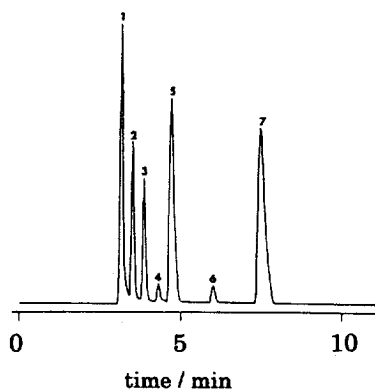


Fig. 10. Separation of inorganic salts on the stationary phase (L-Column ODS, 20×4.6 mm) adsorbing CHAPS. Sample solution containing equimolar (2.857 mM) of peak: 1, NaSO<sub>4</sub>; 2, NaCl; 3, NaBr; 4, NaI; 5, NaSCN; 6, CaI<sub>2</sub>; 7, Ca(SCN)<sub>2</sub>. Mobile phase, water. Detection, conductivity. Reproduction by the permission of the American Chemical Society from Ref. [102].

solution containing NaCl and KBr is injected as a sample, four peaks corresponding to NaCl, NaBr, KCl, and KBr appear at different intensities reflecting the transfer free energies of cations and anions from water to the micellar phase. However, since this will be possible even when monomer surfactants, not micelles, are adsorbed on the stationary phase, it is expected that more detailed mechanisms should be elucidated.

## 5. Conclusion

The micellar chromatography of inorganic compounds, mainly simple ions, has been reviewed. Although most of the retention behaviors of ions can be interpreted on the basis of ion-exchange models, the physicochemical meaning of the model is a little doubtful. For the derivation of more precise and more physically significant equations describing the retention behaviors of ions, improved electrostatic models involving solvation effects should be introduced in chromatographic models. However, such treatments will cause much complication and will not necessarily result in the derivation of a simple and useful equation. In this sense, a simple ion-exchange model would be useful, especially for the prediction and optimization of chromatographic separation.

Multifunctional properties of micelles are also

important for developing novel separation as shown in the last section. In addition, utilization of functionalized micelles, micellar catalysis, the statics and kinetics in micellar media, etc., will give rise to further possibilities in micellar chromatography and allow the design of novel separations. The author does believe that the knowledge of micellar and solution chemistry will permit further developments of micellar chromatography and that further developments of micellar chromatography will bring about developments in micellar and solution chemistry. Micellar chromatography of inorganic ions will surely make a significant contribution because of the simplicity of the interaction involved.

## 6. Symbols

C	a counter ion of a micelle
$C_{aq}$	the concentration of a counter ion in solution
$C_b$	the concentration of a counter ion, bound by micelle, in solution
$C_m$	the concentration of a counter ion in a micellar phase
M	a micelle
$C_M$	the concentration of a micelle in solution
$\bar{V}$	the molar volume of a micelle
$K^m$	the selectivity coefficient in ion-exchange at the interface between a micelle and a solution phase
$K^s$	the selectivity coefficient in ion-exchange at the interface between a stationary and a solution phase
$K_d$	the dissociation constant of counter ions from a micelle
$\alpha$	the dissociation degree of counter ions from a micelle
$P_{MW}$	the partition coefficient of a solute between a micellar and a solution phase
$P_{SW}$	the partition coefficient of a solute between a stationary and a solution phase
$\phi$	a phase ratio

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