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Short Communication

Simultaneous cation and reversed-phase chromatography

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ABSTRACT

Micellar mobile phases facilitate the simultaneous separation of inorganic cations and organic neutral species. With an anionic micellar mobile phase transition metal ions and organic neutral species can be separated, whereas with a non-ionic micellar mobile phase containing a trace anionic surfactant separation of alkali and alkaline earth metal ions can be separated —the elution of alkali or alkaline earth metal ions can be monitored with a conductivity detector, if the trace anionic surfactant incorporated in a mobile phase is used in its acidic form.

INTRODUCTION

A number of advantages of micellar mobile phases over the usual aqueous–organic mobile phases have been pointed out, *e.g.*, non-flammability, non-toxicity, stable baselines and a short reconditioning time for repeated analyses in gradient elution and facilitation of the evaluation of partition coefficients to micellar and stationary phases [1-10]. In addition the easy modelling and prediction of the retention behaviours of ions is an advantage of inorganic micellar chromatography [11], and simultaneous separations of transition metal ions and phenols with anionic micelles have been presented [12].

Although micellar mobile phases facilitate the simultaneous separation of ions and neutral species, there are some problems with detection. With transition metal ions and aromatic organic compounds, selective detection is easy; the former are detectable by applying postcolumn reaction with, *e.g.*, pyridyl azoresorcinol, and the latter by UV absorption. However, it is difficult to detect alkali or alkaline earth metal ions in solutions containing an anionic micelle. To overcome this problem, the use of mixed micellar mobile phases composed of a non-ionic surfactant as a principal component and a trace anionic surfactant has been investigated; the former permits the separation of neutral species and the latter the separation of cations. In this work, simultaneous cation and reversed-phase chromatography using micellar mobile phases was studied and the usefulness of micellar chromatography for such a purpose was reconfirmed.

EXPERIMENTAL

A Tosoh chromatographic system was used, consisting of a CCPD computer-controlled pump, a Rheodyne injection valve, a CO-8000 column oven set at 25°C, a UV-8000 UV detector and a CM-8000 conductivity detector. The separation column was Inertsil ODS (Gaskro Kogyo) of 150 mm × 4 mm

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I.D., packed with octadecylsilylated silica gel of 5 μm particle size. All solutions were prepared with distilled, deionized water. Anionic surfactants were recrystalized from methanol. Other reagents were of analytical-reagent grade and were used as received.

The amounts of surfactants adsorbed in the column were determined with a breakthrough method.

RESULTS AND DISCUSSION

Simultaneous separation and detection of organic neutral species and transition metal ions

As reported previously [11,12], organic neutral species and transition metal ions can be separated with an anionic micellar mobile phase containing appropriate complexing agents such as tartaric acid. In this instance, transition metal ions are detectable by applying a postcolumn reaction using, *e.g.*, pyridylazo resorcinol; organic neutral species, most of which are detectable by UV spectrometry, do not interfere with the detection of transition metal ions, and *vice versa*. Optimization of the separation is therefore performed in a simple manner [12]. The elution of organic neutral species obeys the usual retention model developed by Armstrong [1,2], and that of transition metal ions can be described by an equation involving complex formation and mass action by a counter cation as shown previously [11]. Fig. 1 shows an example of the simultaneous separation of transition metal ions and some aromatic organic compounds with a sodium dodecyl sulphate (SDS) micellar mobile phase containing tartaric acid.

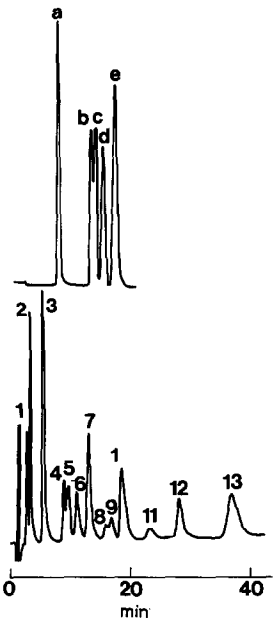

Fig. 1. Simultaneous separation of (top) transition metal ions and (bottom) aromatic neutral species. Mobile phase, 0.1 *M* sodium dodecyl sulphate–0.05 *M* tartaric acid (pH 3.6). Detection, UV at 254 nm for aromatic neutral species and visible at 540 nm for transition metal ions following postcolumn reaction with pyridylazoresorcinol. Peaks: a = Cu^{2+}; b = Zn^{2+}; c = Ni^{2+}; d = Co^{2+}; e = Mn^{2+}; 1 = *p*-hydroxybenzyl alcohol; 2 = resorcinol; 3 = *p*-hydroxybenzaldehyde; 4 = benzyl alcohol; 5 = phenol; 6 = *p*-nitrophenol; 7 = 2-phenylethanol; 8 = *p*-cresol; 9 = acetophenone; 10 = 3-phenyl-1-propanol; 11 = *p*-ethylphenol; 12 = 1-naphthol; 13 = *p*-*tert*-butylphenol.

Simultaneous separation and detection of organic neutral species and alkali and alkaline earth metal ions

The elution of alkali and alkaline earth metal ions cannot be monitored with a postcolumn reaction and another detection method should therefore be considered. Although these ions are usually detected by conductivity in ion chromatography [13,14], conductivity detection has the limitation that the ionic strength of the mobile phase should be low. To separate organic neutral species such as phenols within an acceptable time, 0.05–0.1 *M* surfactant solutions should be used as mobile phases. If the mobile phase contains an ionic surfactant alone, the ionic strength of the solution is too high for conductivity detection to be used for monitoring ions. This problem can be solved as follows.

Non-ionic micellar mobile phases have been successfully used in reversed-phase chromatography, although the poor separation efficiency has been pointed out and its use is not as common as that of ionic micelles [3,4]. Borgerding and Hinze [3] outlined some premises concerning poor separation efficiency when using a non-ionic micellar mobile phase. Non-ionic surfactant molecules adsorbed on the stationary phase cause an increase in the effective film thickness of the stationary phase, produce a more polar stationary phase and disturb the effective mass diffusion of analytes in the stationary phase. In this study, though no enhancement of the separation efficiency was observed, the use of Brij

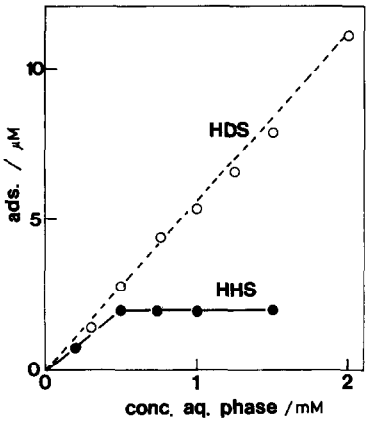

Fig. 2. Adsorption isotherms of HDS and HHS from 0.05 *M* Brij 35 solution to the stationary phase.

35 brought about a significant advantage for the present purpose.

It is obvious that non-ionic micelles do not influence the conductivity detection of ions. Although there remain some questions about the separation performance as stated above, the use of non-ionic micelles containing a trace anionic surfactant permits the conductivity detection of Group 1A and 2A metal ions and the UV detection of neutral species after their simultaneous separation. Fig. 2 shows the adsorption of dodecylsulphuric acid (HDS) and hexadecylsulphuric acid (HHS) in the presence of Brij 35 as a major mobile phase component. The amounts of adsorbed HDS increase linearly with increase in concentration, whereas the adsorption of HHS becomes constant when the concentration reaches *ca.* 0.5 m*M*. An adsorption equilibrium of an ionic surfactant is usually established between the monomeric surfactant and the adsorbed surfactant, and micelles do not participate in the equilibrium. The break point of the adsorption isotherm curve of HHS is therefore due to the formation of the micelle, whereas HDS does not give any break point, suggesting that HDS forms no micelles over this concentration range. Although these anionic surfactants may form mixed micelles with Brij 35, conductivity measurements did not give a clear break point owing to the mixed micelle formation. It is predictable from Fig. 2 that HDS is a better additive than HHS because the low adsorption of HHS causes weak retention and poor resolution.

TABLE I

PARTITION COEFFICIENTS OF ANALYTES BETWEEN WATER AND BRIJ 35 MICELLAR PHASE (K_{MW}) AND BETWEEN WATER AND THE STATIONARY PHASE (K_{SW})

Partition coefficients were determined on the basis of the following equation.

$$1/(V_r - V_0) = [(K_{MW} - 1)\bar{v}_m + 1] / K_{SW} V_s$$

where V_r, V_0 (= 1.56 ml) and V_s (= 1.25 ml) are retention volume, void volume and volume of the stationary phase, $\bar{v}$ is the partial molal volume of the micelle (= 1120 ml/mol for Brij 35 micelles) and C_m is the concentration of micelles.

Analyte	K_{MW}	K_{SW}
Phenol	56.6	46
p-Cresol	145	160
p-Ethylphenol	323	380
p-*tert*-Butylphenol	1100	1850
p-Hydroxybenzaldehyde	52.6	32
Resorcinol	59.2	31
Benzyl alcohol	9.48	6.3
2-Phenylethanol	13.3	10

The non-ionic compounds tested and the partition coefficients are listed in Table I. Partition coefficients between water and Brij 35 micelles were determined on the basis of Armstrong's model. As trace ionic surfactants do not affect the retention of non-ionic compounds, the separation of these neutral species is first optimized using the partition coefficients listed in Table I. The results are shown in Fig. 3, which indicates that 0.043 *M* Brij 35 gives the best resolution. Also, the analysis time, which is determined by the elution of *tert*-butylphenol in this instance, is acceptably short. Therefore, the concentration of Brij 35 was fixed at 0.04 *M* for the following investigation.

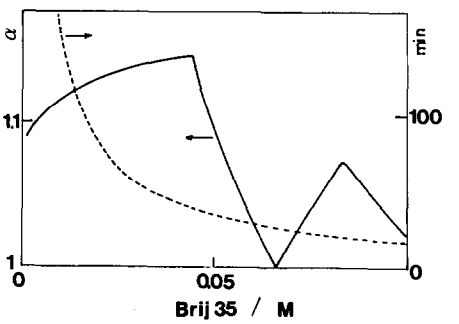

Fig. 3. Simulated changes in minimum separation ratios (solid line) and retention times of *p*-*tert*-butylphenol (broken line) with the concentration of Brij 35.

TABLE II

CHANGES IN RETENTION TIMES OF SELECTED CATIONS WITH THE CONCENTRATION OF HDS IN 0.04 *M* BRIJ 35 MOBILE PHASE

Concentration of HDS (m*M*)	Retention time (min)			
	Na^+	K^+	Mg^{2+}	Ba^{2+}
0.5	2.95	3.15	7.35	10.5
0.75	2.80	3.20	8.25	12.2
1.0	3.0	3.45	8.0	12.0

Table II shows changes in the retention of Na^+, K^+, $Mg2^+$, and Ba^{2+} with the concentration of HDS in 0.04 *M* Brij 35. The retention times are almost constant, and do not vary with the concentration of HDS. This phenomenon can be explained as follows. The capacity factor of a metal ion can be described by

$$k' = \phi\,[M^{n+}]_s/[M^{n+}]$$
$$= \phi\,K_{IE}[H^+]_s^n/[H^{n+}]^n$$

where ϕ is a phase ratio, K_{IE} is the ion-exchange equilibrium constant of $M^{n+} + nH^+(s) \rightleftharpoons M^{n+}(s) + nH^+$ at the stationary phase surface and s denotes the stationary phase. As shown in Fig. 1, the amounts of adsorbed HDS linearly increase with increasing concentration of HDS in the mobile phase, indicating that $[H^+]_s$ is also proportional to the concentration of HDS. $[H^+]$ is also proportional to the concentration of HDS. Therefore, the capacity factor is independent of the concentration of HDS.

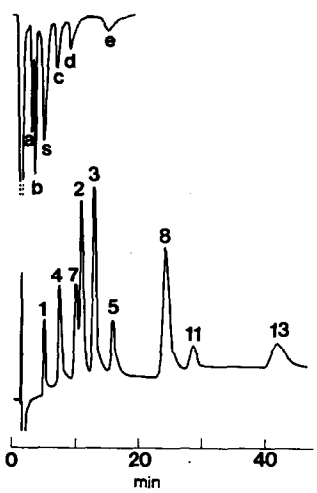

Fig. 4. Simultaneous separation and detection of (top) metal ions and (bottom) aromatic neutral species. Mobile phase, 0.04 *M* Brij 35–0.75 m*M* HDS. Detection, conductivity (10 μS/cm full-scale) for metal ions and UV at 254 nm for organic neutral species. Peaks: a = Na^+; b = K^+; c = Mg^{2+}; d = Ba^{2+}; e = Pb^{2+}; s = system peak; and aromatic compounds as in Fig. 1.

Fig. 4 shows examples of the simultaneous separation of cations and organic neutral species. When HHS was used in Brij 35 mobile phase, the resolution between cations was poorer, as predicted, although the results are not shown. On the other hand, as can be seen in Fig.4, the separation between cations obtained with a Brij 35 mobile phase containing HDS is much better, but still poor in comparison with the usual cation chromatography. Although the poor separation is obviously due to weak adsorption of anionic surfactants in the presence of Brij 35, monovalent cations and divalent cations are simultaneously separated. This is known to be difficult in the usual ion-exchange chromatography.

The present scheme may be applied to the separation and detection of various amines, which are separated with simultaneous partition and ion-exchange modes, and measured by UV and/or conductimetric detection. To accomplish such separations, the low separation efficiency should be overcome by optimizing the mobile phase conditions. This task remains to be studied.

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