

Short Communication

Behaviour of the system peak in ion chromatography with indirect ultraviolet absorption detection and trimellitate as eluent

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ABSTRACT

The behaviour of the system peak has been studied using an ion chromatographic system equipped with an ultraviolet detector and an ODS column coated with cetyltrimethylammonium bromide and trimellitate (pH 4.0). The intensity of the system peak depended on the pH of the sample injected and also on the injected anion concentration, especially for the injection of an acidic anion of high concentration.

INTRODUCTION

In high-performance liquid chromatography (HPLC) or ion chromatography (IC), the injection of a sample into a eluent containing more than one component often causes the appearance of so-called system peaks [1–8] (or dip peaks [9]). Many papers have reported the formation mechanism and the simulation of the first and second system peaks. A first system peak is eluted at the solvent front and is due to ion exclusion of the sample cation from the resin and the elution of water from the sample [3–9]. The peak is referred to as the injection peak and its retention volume coincides with the void volume of the column [3–8].

A second system peak, which is simply called the

“system peak” in this paper, is eluted later and may cause incorrect peak identification and waste time. Many formation mechanisms of this system peak have been discussed, with some computer simulations in IC [4,5,8,9]. It is generally assumed that the system peak mainly results from a eluent-deficient zone formed by the sample injection and also depends on the pH of the injected sample. Samples containing no eluent anion were injected in previous studies [4,5,8,9].

In this paper, the behaviour of the system peak is reported for anion chromatography using trimellitate (TMA, pH 4.0) as the eluent and some anion samples containing TMA with ultraviolet detection.

EXPERIMENTAL

Apparatus and reagents

The IC equipment consisted of a pump (CCPD, Tosoh, Japan), a variable-wavelength ultraviolet de-

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tector (UV-8000, Tosoh), an injector (Rheodyne, USA) with a 100- μ l sample loop, a column oven (CO-8000, Tosoh) and a pen recoder (YEW Type 3066, Yokogawa, Japan)

All chemicals were of analytical-reagent grade, and deionised, distilled water, further filtered through a 0.45- μ m membrane filter, was used throughout. The solutions of anions were prepared from their sodium salts. The eluent of 1 mM TMA was adjusted to pH 4.0 with diluted sodium hydroxide solution and filtered through a 0.45- μ m membrane filter before use. Phthalate, citrate and benzoate as eluents were also compared with TMA.

Dynamically coated columns were prepared using columns (50 \times 4.6 mm I.D.) packed with ODS resin (Capcell Pack C18, AG120, 5 μ m particle size, Shiseido, Japan). The column was coated with cetyltrimethylammonium bromide (CTMABr) as described previously [10]. The ion-exchange capacity of the coated column was about 0.10 mequiv per column for the eluent ion. Regeneration of the column was carried out by washing with methanol and coating with CTMABr. The commercial TSK gel IC anion SW (Tosoh) was also compared with the coated column.

The injected anions (0.4 mequiv l⁻¹ sulphate, nitrate, chloride, acetate and citrate) were dissolved in 1 mM TMA (pH 7.0) and showed a stable injection pH and large relative absorbance of the system peak. The chromatographic conditions used are summarized in Table I.

RESULTS AND DISCUSSION

Effect of eluent TMA concentration

A basic equation (eqn. 1) has been published for IC in terms of the capacity factor (k') and the concentration of the eluent ion (E), if all other chromatographic conditions are constant except the eluent concentration [4].

$$\log k' = -a/b \log [E] + \text{constant} \quad (1)$$

where a and b are the charges on the sample ion and the eluent ion, respectively.

A slope of plots of $\log k'$ versus $\log [E]$ shows the ratio ($-a/b$) of the charges on the sample and eluent ions. Fig. 1 shows the plots of the $\log k'$ versus $\log [TMA]$ in the coated column and the non-coated column. The slopes for the system peak ni-

TABLE I
CHROMATOGRAPHIC CONDITIONS

Column	ODS column coated with cetyltrimethylammonium bromide (CTMABr)
Column temperature	35°C
Flow-rate	1.0 ml min ⁻¹
Detection wavelength	275 nm
Sample loop	100 μ l
Eluent	1.0 mM Trimellitate (TMA)
Eluent pH	4.0
Sample	0.4 mequiv l ⁻¹ of sample anion in 1 mM TMA solution
Sample pH	7.0

trate and sulphate were 0.73, 0.64 and 0.96 in the coated column, respectively. The charge of the TMA eluent ion at pH 4.0 was about 1.6 as calculated from the acid dissociation constant (pK_{a1} 2.52, pK_{a2} 3.85, pK_{a3} 5.20) [11]. The slope for the nitrate (univalent) ion as sodium nitrate, 0.64 of the experimental value, agrees with the theoretical value of 0.62. Similarly, the slopes (0.94, 0.32 and 0.53) of the system peaks for phthalate, benzoate and citrate eluent were also obtained, as shown in Table II. These slopes should theoretically be 1.0 accord-

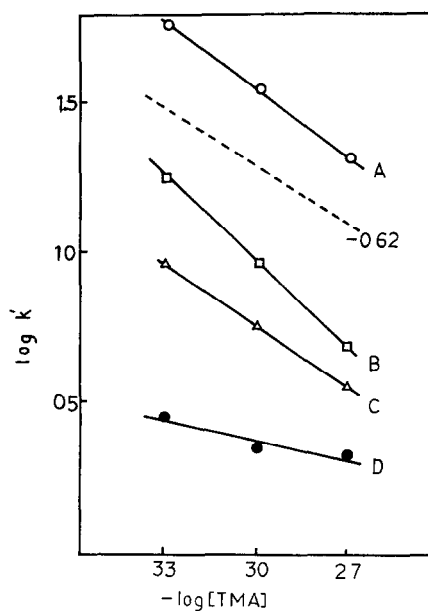


Fig. 1. $\log [TMA]$ versus $\log k'$: (A) System peak, (B) sulphate, (C) nitrate, (D) system peak on non-coated ODS column. Other chromatographic conditions as in Table I.

TABLE II
EFFECT OF ELUENT ON THE SLOPE (a/b)

Equation $\log k' = -a/b \log [E] + \text{constant}$ Eluent concentration 1 mM

Eluent	Eluent pH	Eluent ion charge	Slope ($-a/b$)	
			Nitrate	System peak
TMA	4.0	1.6	0.64	0.73
			—	0.78 ^a
Phthalate	4.3	1.03	0.83	0.94
Citrate	3.6	0.80	—	0.53
Benzoate	4.5	0.67	0.98	0.32

^a Column: commercial TSK gel IC anion SW (Tosoh). The other chromatographic conditions are the same as in Table I.

ing to ion-exchange processes only. However, the experimental values were smaller than 1.0, therefore another process (probably a reversed-phase interaction) must have occurred on the resin. The behavior of system peak observed was similar to that of univalent anion by the two processes (ion exchange and reversed phase interaction) for TMA and phthalate eluents. The slope ($-a/b$) of the system peak for the non-coated ODS column was 0.22. This value also suggests that another interaction occurred on the

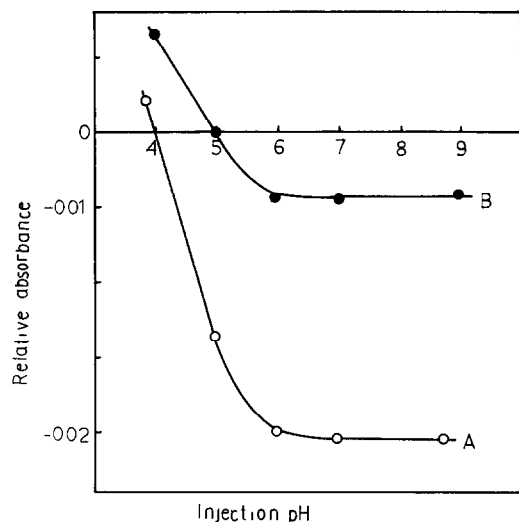


Fig. 2. Effect of injection pH on the relative absorbance of system peak. Eluent (A) 1 mM TMA (pH 4.0), (B) 1 mM TMA (pH 5.0). Sample 1 mM TMA. Other chromatographic conditions as in Table I.

ODS resin in addition to ion exchange. It was found that nitrate and sulphate were not retained on the non-coated column.

Effects of eluent pH and injection pH

The retention times of sulphate and chloride decreased with increasing eluent pH from 4.0 to 6.0 and levelled off at pH values greater than 6, whereas that of the system peak rapidly increased at pH 4.0–5.0 and then disappeared at pH values greater than 6.0.

The effect of the injection pH on the relative absorbances of the system peak and some anions was examined in the pH range 4.0–9.0. The results obtained for the relative absorbance of the system peak are shown in Fig. 2. The system peak appeared as a negative peak when the injection pH was higher than the eluent pH (pH 4.0), whereas the system peak appeared as a positive peak when the injection pH was lower than the eluent pH. The relative absorbance of a negative or positive system peak increased with increasing difference between the injection pH and the eluent pH, although the relative absorbances of the anions did not vary for any injection pH. The absorbance of 1 mM TMA decreased with increasing pH at 275 nm and showed no decrease at pH values greater than 6.0. It is considered that the system peak results from the elution of the TMA band at increased pH (greater than pH 4.0) around the sample zone by sample injection (greater than pH 4.0) into the eluent (pH 4.0). The relative absorbances of the system peak in an aqueous solution and 1 mM TMA solution, the pH equal to the pH of the aqueous solution, pH 4.0 and pH 7.0, are shown in Table III. The relative absorbances of the anions show little variation. It is clear that the presence of TMA in the sample and the difference in pH between the sample and the eluent strongly affects the intensity of the system peak. The intensities of the system peaks by injection of the aqueous sample are smaller compared with those following injection of the sample containing TMA (pH equal to the aqueous solution pH).

Effect of injected sample concentration

The effect of the injected sample anion concentration on the relative absorbance of the system peak obtained by the injection of TMA and some anions was examined in the injected anion concentration

TABLE III
EFFECT OF SAMPLE SOLVENT ON THE RELATIVE ABSORBANCE OF THE SYSTEM PEAK

The chromatographic conditions are as shown in Table I

Anion	Solvent	Sample pH	Relative absorbance
None	1 mM TMA	7.0	0.024
	1 mM TMA	4.0	0.002
Acetate	1 mM TMA	6.6	0.028
	Aqueous	6.6	0.010
	1 mM TMA	4.0	0.001
Chloride	1 mM TMA	7.0	0.022
	1 mM TMA	5.6	0.015
	Aqueous	5.6	0.004
	1 mM TMA	4.0	0.002
Sulphate	1 mM TMA	7.0	0.022
	1 mM TMA	5.8	0.019
	Aqueous	5.8	0.003
	1 mM TMA	4.0	0.002

range 0–10 mequiv l⁻¹. The results obtained are shown in Fig. 3. The relative absorbances of the negative system peak from acetate, citrate and TMA injections increased with increasing concentration of the injected anion, whereas those from chloride and sulphate injections gradually decreased. On injection of more than 0.6 mequiv l⁻¹ sulphate, a positive system peak appeared just in front of the negative system peak usually observed, as shown in Fig. 4, and the relative absorbance of the positive system peak increased with increasing concentration of the injected sulphate. This positive system peak may result from the excess of TMA excluded by the sample injection, as shown in Fig. 4 (lines A and C). A positive system peak also appeared at high concentrations (tens of mequivalents per litre) of chloride. The same phenomena were also observed by using a commercial TSK gel IC anion SW column. The negative system peak was obtained by the injection of hydrogencarbonate, phosphate, acetate and hippurate, and positive and negative system peaks were obtained by chloride and sulphate injections.

Injections of anions with an acid dissociation constant (pK_a) [12] of more than 4.0 (the eluent pH value), such as acetate (pK_a 4.76), citrate (pK_{a1} 4.76, pK_{a2} 6.40) and phosphate (pK_{a1} 7.20, pK_{a2} 12.35),

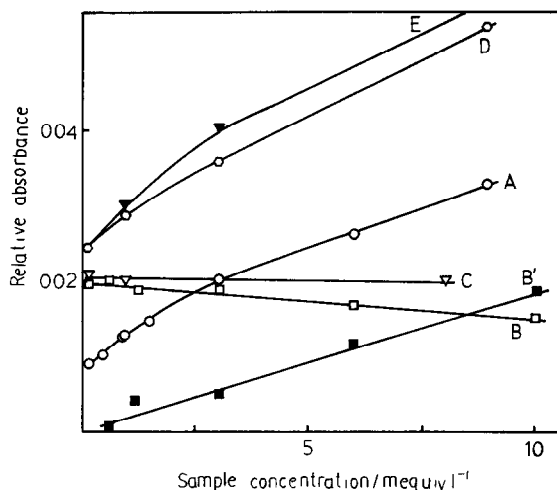


Fig. 3 Effect of sample concentrations on the relative absorbance of system peak. Negative system peak on the injection of (A) TMA, (B) sulphate, (C) chloride, (D) acetate, and (E) citrate. (B') Positive system peak by injection of sulphate. Other chromatographic conditions as in Table I.

and those of less than 4.0, such as chloride and sulphate (pK_{a2} 1.99), give negative system peaks and both positive (at high concentrations) and negative system peaks, respectively. For the injection of the latter, when the sample anion (pH 7.0) was added the low pH eluent (pH 4.0), the charge of the sample anion did not vary, whereas that of TMA around the sample zone changed and the local pH of TMA

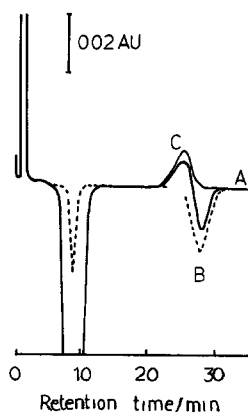


Fig. 4 Chromatogram of system peak. System peak on the injection of (A) (solid line) 5 mM sulphate, (B) (broken line) 0.2 mM sulphate, (C) (fine line) 4 mM TMA (pH 4.0). Other chromatographic conditions as in Table I.

became higher than 4.0. The combination of a negative and positive contribution to the intensity of the system peak due to the higher pH and the excess of TMA by sample injection may explain the appearance of negative and positive system peaks. However, the charges of sample anion and TMA were affected by the injection, the charge of sample anion decreased, the charge of TMA became higher than that of eluent TMA and then the local TMA became more basic. When the basic TMA was eluted, only a negative system peak appeared. The contribution of the excess TMA by sample injection was smaller than that of pH. The intensity of the negative system peak only became larger for an injected anion with a basic pK_a value.

It was confirmed that system peak resulted from the elution of local TMA when the pH was varied by sample injection. The intensity of the system peak depended greatly on the difference in pH between the injected sample containing the eluent anion and eluent, and also on the injected anion

concentration. The profile of the system peak on the chromatogram was varied by the injection of an acidic anion of high concentration.

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