Short communication

Ultrasonic effects on ion-exchange chromatographic retention

Tetsuo Okada

Department of Chemistry, Tokyo Institute of Technology, Meguro-ku, Tokyo 152, Japan

Abstract

Ultrasound radiation has been studied as a possible novel parameter to control ion-exchange chromatographic retention of some simple ions. Though the reason has not been elucidated, ultrasound radiation has reduced the retention for the larger and less solvated ions but enhanced the retention of the smaller and more solvated ions. The adsorption amounts of weak acids have been also affected by ultrasound radiation. © 1998 Elsevier Science B.V.

1. Introduction

External fields promise the enhancement of separation selectivity and additional versatility for various separation techniques such as chromatography, electrophoresis, membrane separation, etc. Electric [1–3], magnetic [4], optical [5] and temperature [6] fields have been investigated for this purpose, and have proved to be effective separation parameters. In chromatography, for example, the interaction of solutes with a stationary phase is the primary retention mechanism, basically chemical equilibria. In contrast, the interaction with an external field is mostly a physical process, and the extent of the interaction can be externally controlled, e.g. without changing mobile phase compositions. Thus, the external fields have recently been well investigated as a novel parameter to control the retention.

In the present communication, the author pays his attention to ultrasound as a novel external field in ion-exchange chromatography. Some effects are expected by ultrasound radiation, e.g. cavitation, ultrasonic vibration potential (Debye potential), vol-

ume relaxation etc. [7]. The cavitation will cause local increases in the pressure and the temperature. The Debye potential and volume relaxation are related to solute sizes in solution, which are among the most important factors governing the overall separation selectivity in ion-exchange chromatography. Thus, ultrasound is expected to modify the ion-exchange separation selectivity. Enhanced mixing by ultrasound radiation was expected as a method alternative to mechanical stirring in ion-exchange experiments [8,9], and enhanced selectivity for Cl^- over NO_3^- was reported [9]. However, thorough experiments have not been reported. Chromatography is advantageous over batch experiments to elucidate ultrasound effects on ion-exchange selectivity.

2. Experimental

The chromatographic system was composed of a Tosoh model computer-controlled pump CCPD, a Tosoh model conductivity detector CM-8000, a

Tosoh model UV–Vis detector UV-8010, a Rheo-
dyne injection valve equipped with a 100 μl sample
loop, and a chart recorder. Ultrasound was provided
by an ordinary ultrasonic bath (Branson model
B-220J, output power 60 W and vibration frequency
47 kHz). The temperature in the ultrasonic bath
was kept at 25°C. The flow-rate was 1.0 ml min^{-1}.
Separation columns were TSKgel IC-Anion-PW and
TSKgel IC-Cation (particle size 10 μm, packed in
4.6 mm I.D.×50 mm PTFE column for both).
Reagents used were of analytical grade. Mobile
phases and sample solutions were prepared in dis-
tilled deionized water. The column void volume was
measured from a water peak detected with the
conductivity detector. Measurements were duplicated
or triplicated.

3. Results and discussion

Fig. 1 shows selected examples of separation of
anions with and without the radiation of ultrasound,
where BrO_3^-, NO_2^- and NO_3^- were selected as solute
anions and tartaric acid was used as an eluent.
Though the difference in retention between with and
without the ultrasound radiation is so small that one
may fail to find a significant change, numerical
values obviously indicate decreases in retention
times. Table 1 lists retention times without ultra-
sound radiation and effects of ultrasound radiation
(as relative k') with varying pH of tartaric acid
eluents. Though ultrasound radiation basically re-
duces the retention, stronger effects are seen for
solute ions having larger affinity to ion-exchange
resin than for those having smaller affinity; the
reduction of k' is ca 3%, 6% and 10% for BrO_3^-,
NO_2^- and NO_3^-, respectively (the affinity to anion-
exchange resins is enhanced in this order). Thus, it
appears that effects of ultrasound radiation depend
not on the retention time but on a particular nature of
solute ions. Similar phenomena were observed for
cation-exchange chromatography, where H^+ was
used as an eluent and some alkali metal ions were
separated. Effects (decreases in retention times)
become small in the order $Cs^+ > K^+ > Li^+$. Both in
anion-exchange and in cation-exchange chromatog-
raphy, an ion of larger ion-exchange affinity in
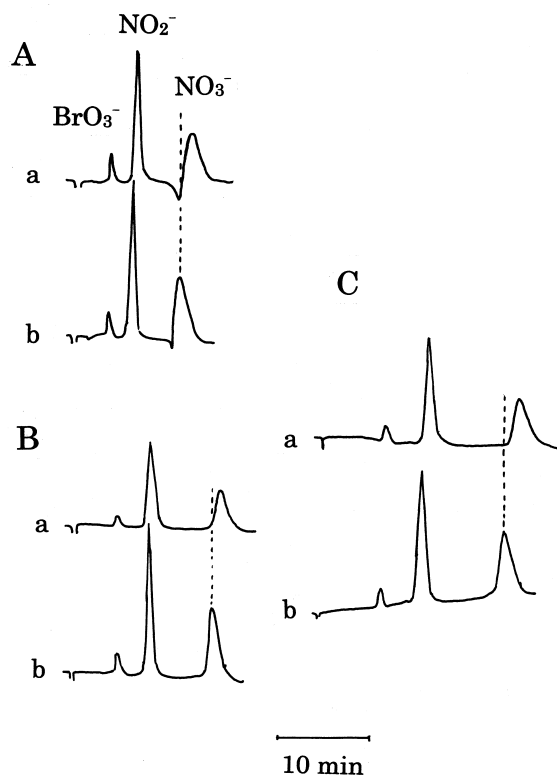nature receives stronger effects from ultrasound.

Fig. 1. Ultrasound effects on retention times: A, eluent, 1 mM
tartaric acid (pH 4.4); B, eluent, 0.5 mM tartaric acid (pH 4.4); C,
eluent, 0.2 mM tartaric acid (pH 4.4); (a) without ultrasound
radiation; (b) with ultrasound radiation.

The origin of ion-exchange selectivity has been an
important issue in separation of ionic compounds
[10]. No one doubts that it comes from several
mechanisms rather than from a single mechanism
and that the sizes (or solvated volumes) of ions can
be closely related to ion-exchange selectivity; usual-
ly, the more solvated ions are less preferably retained
by ion-exchange resin than less solvated counter-
parts. The above results suggest that effects of the
ultrasound radiation may also be related to the
solvation of solute ions; the relative ion-exchange
affinity of less solvated ions is reduced, while that of
more solvated ions is enhanced.

In order to more clearly show this effect of
ultrasound radiation in ion-exchange, we selected
two anions, Cl^- and ClO_4^- as a more solvated weak
eluent and a less solvated strong eluent, respectively.
IO_3^- was selected as a solute for ClO_4^- eluents

Table 1
Effects of the radiation of ultrasound in anion-exchange chromatography with tartaric acid eluents

pH of eluents[a]	Relative k'[b]		
	BrO_3^-	NO_2^-	NO_3^-
3.24	0.98 (13.3[c])		
3.32	0.97 (12.3)		
3.43	0.98 (11.0)	0.95 (12.7)	0.89 (38.3)
3.55	0.95 (8.9)	0.92 (11.7)	0.90 (31.2)
3.70	–[d]	0.95 (10.6)	0.91 (25.2)
3.87	0.98 (6.0)	–	0.93 (21.0)
4.08	0.96 (5.0)	0.96 (8.1)	0.91 (17.2)
4.28	0.97 (4.0)	0.94 (6.7)	0.89 (13.1)
4.59	0.97 (3.2)	0.96 (5.6)	0.91 (10.2)
4.90	0.97 (3.1)	0.93 (4.5)	0.90 (8.0)

[a] 1 mM tartaric acid.
[b] Ratio of k' with ultrasound radiation to that without radiation. k' values were calculated in terms of a water peak, and the retention of water was not changed with ultrasound radiation. Though k' should be calculated from the peak gravity, the peak top was used for listed values because of negligible differences in relative k' values.
[c] Corrected retention time without ultrasound radiation in min.
[d] Not measured.

because of the very low affinity of IO_3^- to anion-exchange resins, and NO_2^-, NO_3^- and I^- were selected as a solute for Cl^- eluents. The usual anion-exchange selectivity increases in the order of $IO_3^- < Cl^- < NO_2^- < NO_3^- < I^- < ClO_4^-$. Results are summarized in Table 2. With ClO_4^- eluents, k' values (or corrected retention times) are increased by ca. 5% irrespective of the eluent concentration (or retention times). In contrast, k' values of solutes with Cl^- eluents were reduced to the extent dependent on the nature of solute anions; I^- is most affected, and NO_2^- the least. Thus, the ultrasound radiation in

Table 2
Changes in retention with ultrasound radiation

Eluent	Solute (relative k'[a])
0.32 mM ClO_4^-	IO_3^- (1.05)
0.2 mM ClO_4^-	IO_3^- (1.05)
0.16 mM ClO_4^-	IO_3^- (1.05)
0.1 mM ClO_4^-	IO_3^- (1.04)
6.95 mM Cl^-	NO_2^- (0.98)
	NO_3^- (0.95)
	I^- (0.92)

[a] Ratio of k' with ultrasound radiation to that without radiation.

ion-exchange chromatography is closely related to the solvation states of ions.

Another interesting feature of ultrasound radiation in ion-exchange was observed in the cases where eluents of weak acids go through the pH-dependent dissociation. Some typical detector outputs obtained with tartaric acid eluents are illustrated in Fig. 2. The baseline monitored with either a UV or a conductivity detector was changed by ultrasound radiation; tartaric acid was desorbed by ultrasound radiation, but similar (but a little smaller) amount of tartaric acid is adsorbed again by the resin when stopping ultrasound radiation. Results are summarized in Table 3, where the desorption caused by ultrasound radiation and adsorption for reequilibration by turning the radiation off were quantified on the basis of conductivity data; for the calculation of these amounts, constant pH of effluents was assumed. Adsorption amounts reduced by ultrasound radiation are changed with pH of eluents. It appears that reduced adsorption is related to the concentration of monovalent tartrate species, because the maximum effect can be seen at pH=ca. 3.55 where the first dissociation of tartaric acid is almost completed and
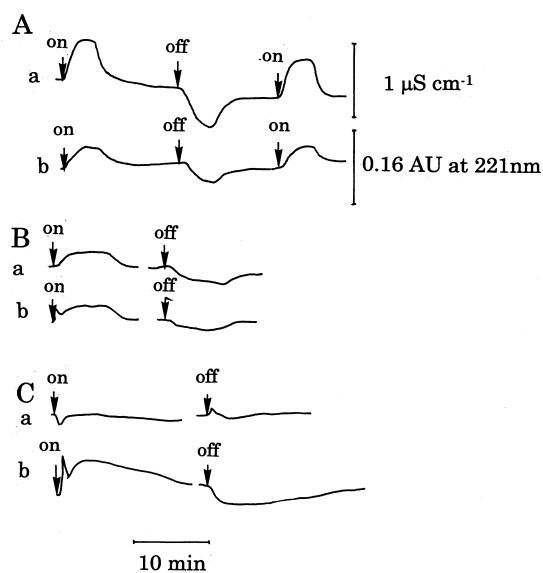

Fig. 2. Ultrasound effects on the ion-exchange equilibria of tartaric acid solution. A, 1 mM tartaric acid (pH 3.24); B, 1 mM tartaric acid (pH 3.87); C, 1 mM tartaric acid (pH 4.59); (a) conductivity detector output; (b) UV detector output.

Table 3
Reduction of amounts of adsorbed tartrates by ultrasonic radiation

Eluent[a] pH	Adsorbed (or desorbed)/nmol		
	Ultrasonic on	Ultrasonic off	Time for reequilibration/min
3.24	−6.30[b]	5.69	5.5
3.32	−10.9	8.93	6.5
3.43	−12.1	10.4	7.5
3.55	−14.6	9.77	8.0
3.70	−10.7	7.15	8.5
3.87	−9.79	7.44	9.0

[a] 1 mM tartaric acid solution.
[b] Changes in adsorbed amounts were calculated from the conductance of an eluent.

the relative concentration of the monovalent species is highest. There are two possible explanations for this phenomenon. The first explanation is that the pH of the solution shifts by ultrasonic radiation. Such shift will be possible because the ultrasonic radiation change the relative stability of dissolved species. The second one is the consideration similar to the above explanation of ultrasound effects on ion-exchange selectivity. The divalent tartrate ion is more solvated than the monovalent species due to the higher charge density of the former. Since, as mentioned above, ultrasound radiation enhances the affinity of well solvated species relative to less solvated species, the relative affinity of the divalent species to the ion-exchange resin will become stronger than mono-valent species by ultrasonic radiation. Thus, the ultrasound radiation causes apparent desorption of tartaric acid on the anion-exchange resin, though the reason is not clear. Similar phenomena were ob-served for carbonate and phosphate eluents.

The important effects of ultrasound in chemistry are separated into several categories; (1) volume relaxation, (2) Debye potential, and (3) cavitation. The volume relaxation and the Debye potential may cause the change in ion-exchange selectivity. How-ever, the frequency used in the present case might be too low for these phenomena to occur in the ion-exchange column. The redistribution of ionic solute by the Debye potential occurs according to the wavelength of the ultrasound. The wavelength of the ultrasound of 47 kHz should be 3.16 cm because the sound velocity is 1483 ms^{-1} in water at 20°C. This wavelength is much longer than the particle size of the resin by four orders of magnitude or the thick-ness of an electrical double layer by more than five

orders of magnitude. The volume relaxation is related to the reaction rate; ion-exchange or equilib-ria in solution should occur much faster than the ultrasound time scale (21 μs).

Cavitation produces local high pressure and tem-perature, enhances reaction kinetics, and has thus been utilized in, for example, organic syntheses [11] and electrochemistry [12]. Cavitation occurs with the radiation of ultrasound at lower frequencies, possibly at 47 kHz used in the present study. However, the pressure inside the separation column is higher than the atmospheric pressure, which possibly makes cavitation difficult. Although we could not verify the occurrence of the cavitation for the present case, it possibly causes local high pressure and high tem-perature and results in changes in ion-exchange selectivity.

Temperature increases inside the column are thus a possible mechanism of the observed phenomena. The temperature inside the column was measured with a thermistor both under ultrasound radiation and irradiation. Since the radiation of ultrasound caused a very small increase in the temperature (only ca. 0.05°C), the increase in the bulk temperature was successfully suppressed by immersing the column in thermostated water. The temperature effects on the ion-exchange chromatographic retention were also studied. Increasing temperature resulted in similar results shown above as ultrasound effects; the re-tention of small and highly solvated ion is enhanced with increasing temperature, and vice versa. At least 6°C increase in the temperature was necessary to cause 8% decrease in the retention of I$^-$ with Cl$^-$ eluents as well as 5% increase in the retention of IO$_3^-$ with ClO$_4^-$ eluents. However, more than 20°C

increase was necessary to obtain the same enhancement rate for NO_2^- and NO_3^- retention as listed in Table 2, albeit ultrasound effects on these are also basically marginal.

Thus, though we have not completely elucidated a proper mechanism of ultrasound effects on ion-exchange behaviors of ions, the local microscopic temperature increase (not bulk temperature) is a possible cause of the presented phenomena. The hydration enthalpy is more negative for small and well hydrated ions (e.g. Cl^- or IO_3^-) than for large and poorly hydrated ions (I^- or ClO_4^-), suggesting that increasing temperature shifts the hydrated energies of the former to more positive values. Therefore, it is reasonably inferred that this unstable hydrated states produced by ultrasound radiation are favorable for the interaction of the ion with ion-exchange sites. This discussion may hold for the cases involving acid–base dissociation. Hence, though there are some ambiguities in mechanisms, ultrasound gives further possibility for the external control of chromatographic retention.

Acknowledgements

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