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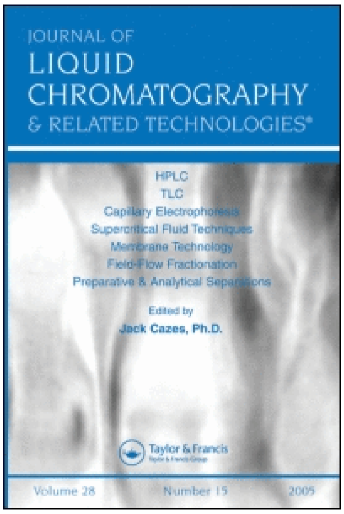

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ENTHALPY-ENTROPY COMPENSATION OF OCTYLSILICA STATIONARY PHASE IN REVERSED-PHASE HPLC

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ABSTRACT

Enthalpy-entropy compensation has been investigated in reversed-phase high performance liquid chromatography with octylsilica stationary phase. The compensation temperatures were determined for this system, and the results show that their change with the composition of the mobile phase was almost similar to that with octadecylsilica stationary phase. It is concluded that the retention mechanism of the separation of alkylbenzenes in both systems with the mobile phase exceed 20 % water content is the same.

INTRODUCTION

The selection of satisfactory separation conditions still remains a major problem in high performance liquid chromatography (HPLC). In recent years, the role of column temeprature in HPLC has been recognized (1-11) and we have reported improved separation with a relatively low temperature column in micro-HPLC and suggested the importance of low

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temperature influence for the separation of thermally labile compounds (8-12).

In these works, we took an enthalpy-entropy compensation approach (4, 11-14). Linear enthalpy-entropy compensation in liquid chromatography has been investigated and some results suggest that an enthalpy-entropy compensation can demonstrate the identity of the retention mechanism underlying reversed-phase separation systems. Since compensation behavior is generally attributed to the effect of the solvent on the interacting species, comparison of the compensation temperature obtained with appropriate data can serve as a diagnostic tool for variations in the retention mechanism on changing the conditions such as the mobile phase composition and column temperature. In the previous work (12) we have demonstrated that enthalpy-entropy compensation occurs in the low temperature reversed-phase micro-HPLC with octadecylsilica stationary phase. This short contribution describes the application of the enthalpy-entropy compensation approach to investigate the reversed-phase system with octylsilica stationary phase and to evaluate the similarity of the retention mechanism in both systems.

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EXPERIMENTAL

A model MF-2 microfeeder (Azuma Electric, Co.Ltd., Tokyo, Japan) was used as the pump. The detector was a Jasco Uvidec 100-III UV spectrophotometer set at 207 nm. The column used was prepared by packing a 0.5 mm i.d. x 12.6 cm long PTFE tubing with octylsilica bonded material (FineSIL, C-8, 10 um, Jasco) by the slurry technique.

The temperature of the column was controled by a Komatsu DW-620 thermostat (Tokyo,Japan). The temperature range examined was from - $1^{o}C$ to $50^{o}C$.

The eluents used were as follows; acetonitrile/water: water content 0.1 %, 10 %, 20 %, 30 %. A HPLC grade acetonitrile was purchased from Kanto Chemicals (Tokyo, Japan). Water was purified and distilled. The test substances (alkylbenzenes) were obtained from Tokyo Kasei (Tokyo, Japan).

Prior to measurements the column was washed with the mobile phase until a constant value for the retention volume of the test substances was obtained. The test substances were injected into the column as 1000 ppm solution in each mobile phase. For t_0 measurements, sodium nitrite of 100 ppm (15, 16) water solution was used. The capacity factor, k', was calculated by the normal way such as $k'=(t_R-t_0)/t_0$ in which t_R is the retention time of a solute. All measurements were made in triplicate. The average reproducibility was better than 0.3 %.

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RESULTS AND DISCUSSION

In the enthalpy-entropy compensation as described by Melander et. al.(4), a plot of ln k' against 1/T (van't Hoff plot) yields a straight line if the mechanism of the process is the same over the temperature range investigated and the enthalpy is constant.

$$\ln k' = -\Delta H^o/RT + \Delta S^o/R + \ln\phi \qquad (1)$$

where ϕ is the phase ratio of the column.

The plots obtained for alkylbenzenes are indeed linear and the slopes are positive; hence, for these substances in the system with octylsilica the enthalpy is constant and negative over a temperature range investigated. The regression coefficients are listed in Table-1.

To calculate the compensation temperature β , following equation was used;

$$\ln k'_T = -\Delta H^o(1/T - 1/\beta)/R - \Delta G^o/R + \ln\phi \qquad (2)$$

Table-1 Data of the van't Hoff plots for alkylbenzenes.

water content in mobile phase	ΔH^{o}, kcal/mole ethyl-benzene	n-butyl-benzene	n-hexyl-benzene	n-octyl benzene
0.1 %	1.504 (0.927)	1.417 (0.971)	1.596 (0.956)	1.638 (0.961)
10 %	0.656 (0.960)	0.836 (0.966)	0.893 (0.991)	1.394 (0.981)
20 %	1.021 (0.983)	0.983 (0.942)	1.286 (0.999)	1.502 (0.974)
30 %	0.676 (0.961)	0.845 (0.983)	1.253 (0.989)	1.411 (0.977)

The number in a parenthesis shows the regression coefficient for each instance.

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where k'_T is the capacity factor at temperature T. The temperature T should be near the harmonic mean of the experimental temperatures used for the evaluation of the enthalpies and 293 K is used in this investigation.

After the data have been replotted according to the equation-(2), it is confirmed that the enthalpy-entropy compensation occurs in all the instances investigated. The calculated compensation temperatures are summarized and compared with those with octadecylsilica stationary (12) phase in Table-2.

Identity or close similarity of the compensation temperatures would strongly suggest that the retention mechanism is the same under the conditions examined.

The results shown in Table-2 are almost similar to those with octadecylsilica stationary phase system, and provide the following information items;

1) the compensation temperature is dependent on the water contents of the mobile phase.

Table-2 Compensation temperatures.

water content in mobile phase	compensation temperature, β , K	
	octylsilica	octadecylsilica
0.1 %	360(293)	381(273)
10 %	464(293)	517(278)
20 %	586(292)	639(278)
24 %	-	682(293)
30 %	721(293)	-
ref.4	639(-)*	
ref.13	794(-)**	

The number in a parenthesis is k'_T for each instance.

* methanol/water system with Pharmaphase ODS for substituted benzene derivatives.

** methanol/water system with octylsilica and octadecylsilica for heptylbenzoates homologues.

2) the compensation temperature increases with increasing water contents of the mobile phase.

3) the compensation temperatures are almost similar to those in normal phase system (385 K in n-hexane-silica system (4) and 480 K in FC-78-silica system (11)) at the water content lower than 10 % in mobile phase.

4) the compensation temperature of 586 K and 721 K for water content of 20 % and 30 % in the aqueous mobile phases, respectively, are consistent with the values of 639 K and 794 K described for other reversed-phase systems.

From above four information items, it is concluded that the retention mechanism with octylsilica-aqueous mobile phase system is almost the same to that with octadecylsilica-aqueous mobile phase system. This has been confirmed by the different experimental ways in elsewhere (17).

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The reversed-phase mechanism (e.g., solvophobic theory or sorption theory) contributes to the retention of alkylbenzenes in both systems of octyl- and octadecylsilicas stationary phases where the water content of the aqueous mobile phase exceed 20 %, otherwise very similar to the mechanism in the normal phase systems at lower water content in the mobile phase, although the chromatographic data shown here does not prove whether the interactions are directly with the reversed-phase (solvophobic theory) or with solvent molecules absorbed on the surface of the reversed-phase (sorption theory).

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