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EFFECT OF DENSITY ON ENTHALPY AND ENTROPY OF TRANSFER FOR SUPERCRITICAL FLUID CHROMATOGRAPHY

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SUMMARY

The effect of density on the enthalpy of transfer and the entropy of transfer of the solute between the mobile and stationary phase was investigated for capillary supercritical fluid chromatography (SFC) using carbon dioxide as the mobile phase. The solutes were *n*-alkanes and *n*-alkanols and the stationary phases were coated *in-situ* cross-linked SE-54 and OV-17. Enthalpies were seen to decrease as fluid density increased over a range of 0.20 to 0.50 g/cm³. The range of enthalpies were from -5.9 to -8.4 kcal/mol for OV-17 and -3.9 to -8.6 kcal/mol with SE-54. The entropy ranged from -7.1 to -16.2 cal/mol · K for SE-54 and -12.5 to -17.0 cal/mol · K for OV-17. The results demonstrate the interdependence of enthalpy and entropy of transfer with supercritical fluid density during chromatographic separations.

INTRODUCTION

The retention mechanism in supercritical fluid chromatography (SFC) is complex. An extra dimension of difficulty facing the separation scientist is contributed by the volume expansivity or isothermal compressibility of the supercritical fluid in the column under isobaric or isothermal conditions, respectively¹⁻⁴. Fluid density is controlled by the state variables of temperature and pressure, allowing one to modify solute retention. Solute retention in SFC has been studied for a large number of solute molecules over a range of fluid densities⁵⁻¹³.

Solute retention in SFC is dependent on the free energy of transfer of the solute from the mobile to the stationary phase. The partitioning process between the two phases is a combination of two thermodynamic contributions; enthalpy and entropy. The enthalpy of solute partitioning can be obtained over an appropriately narrow range of temperature from the slope of a plot of the natural logarithm of solute retention ($\ln k'$) versus reciprocal temperature at constant density¹⁴. The enthalpy of solute transfer (ΔH_T^0) between the two phases at infinite dilution is a basic thermochemical parameter which can be used to understand and predict retention in SFC. The density range of reported ΔH_T^0 values have been limited and no systematic study has been reported to date^{14,15}.

The purpose of this work is to report the variation in ΔH_T^0 and the entropy of transfer ΔS_T^0 as a function of density over a range of 0.20 to 0.50 g/cm³ for carbon dioxide with a series of solute probes using coated, *in-situ* cross-linked capillary columns. This range of densities allows one to gain a more general understanding of the effect of density on retention in SFC.

THEORY

At equilibrium solute retention in SFC can be defined by

$$\Delta G_T^0 = -RT \ln K_D \quad (1)$$

where ΔG_T^0 refers to the change in Gibbs free energy of solute transfer from unit molar concentration in the mobile phase to a hypothetical unit molar concentration of solution in the stationary phase¹⁶, K_D is the solute distribution coefficient, while R and T are the gas constant and temperature, respectively.

The thermodynamic relationship between the free energy and enthalpy and entropy is

$$\Delta G_T^0 = \Delta H_T^0 - T\Delta S_T^0 \quad (2)$$

where ΔS_T^0 is the change in entropy of solute transfer. Substitution of eqn. 2 into 3 and rearranging one obtains

$$\ln K_D = -\Delta H_T^0/RT + \Delta S_T^0/R \quad (3)$$

The solute distribution coefficient can be related to solute retention (k') by

$$K_D = C_s/C_m = k'(V_m/V_s) = k'/\varphi \quad (4)$$

where C_s and C_m are the solute concentrations in the two phases, V_m is the volume of the mobile phase and V_s is the volume of the stationary phase. Their ratio φ is defined in this case as the phase ratio. Solute retention, k' , can be determined by

$$k' = (t_R - t_0)/t_0 \quad (5)$$

where t_0 is the elution time of a non-retained peak and t_R is the retention time of the solute. Upon substitution of eqn. 4 into 3 and rearranging,

$$\ln k' = -\Delta H_T^0/RT + \Delta S_T^0/R + \ln \varphi \quad (6)$$

the slope of a plot of $\ln k'$ against $1/T$ at constant density (ρ) yields,

$$(\partial \ln k' / \partial 1/T)_\rho = -\Delta H_T^0/R \quad (7)$$

Therefore the enthalpy of transfer can be obtained experimentally for a set of solutes at different densities by determining solute retention as a function of temperature at constant density. The entropy of transfer can be determined from the intercept of the

plot of eqn. 6, if the phase ratio can be estimated. The reference state in both the mobile phase and stationary phase is the solute at infinite dilution, therefore solute-solute interactions do not influence the standard state. The standard states for both ΔH_T^0 and ΔS_T^0 , based on the concentration units for the distribution coefficient in eqn. 4, is unit molar concentration for both the mobile and stationary phase¹⁶.

EXPERIMENTAL

The experimental apparatus and procedures have been described in detail elsewhere^{17,18}. The enthalpies and entropies of transfer (ΔH_T^0 , ΔS_T^0) for the *n*-alkanes; *n*-heptadecane, *n*-octadecane and *n*-nonadecane (Alltech Assoc.) and *n*-alkanols; *n*-pentadecanol, *n*-hexadecanol and *n*-octadecanol (Wilmad Glass) were obtained for two capillary columns coated with a cross-linked OV-17 and SE-54 stationary phase over a density range of 0.20 to 0.50 g/cm³ for supercritical carbon dioxide. The capillary columns used in this study were 20 m × 50 μm I.D. fused silica, coated with stationary phase, followed by *in-situ* cross-linking to decrease solubility in the supercritical fluid. The stationary phase film thickness for the two columns was calculated to be *ca.* 0.25 μm from the known volume used in coating the columns.

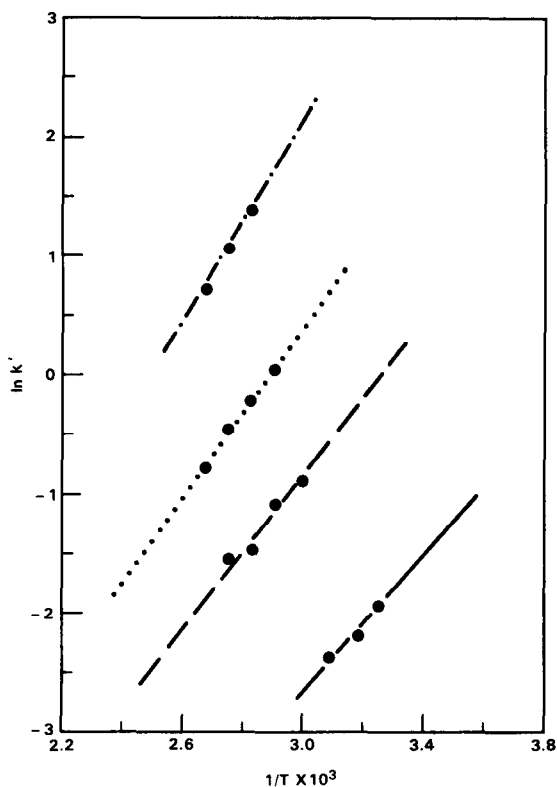


Fig. 1. Plots of $\ln k'$ versus $1/T$ for octadecane. Densities: —, 0.50 g/cm³; ---, 0.38 g/cm³;, 0.30 g/cm³; - · - · -, 0.20 g/cm³. The stationary phase is OV-17.

In the chromatographic studies a Varian 8500 syringe pump operated under computer control was used providing precise control of the fluid density. Retention times of the solutes were determined by a reporting integrator with an accuracy of a tenth of a second. The restrictor at the column outlet was inserted into the inlet of an flame ionization detector for solute detection.

RESULTS AND DISCUSSION

Representative Van 't Hoff plots ($\ln k'$ versus $1/T$) of the different stationary phases for octadecane and octadecanol are shown in Figs. 1-3. The slopes of the plots in these figures allow one to determine the enthalpy of transfer for the solute between the mobile and stationary phase and the entropy of solute transfer from the intercept. Solute enthalpies for the studied density ranges are listed in Tables I and II.

The enthalpies reported here for SFC are quite reasonable when compared to the literature and are generally intermediate between those for liquid and gas chromatography^{14,19-23}. The data in Tables I and II show, as expected, that as retention increases with chain length, ΔH_T^0 becomes more negative. Lauer *et al.*¹⁴, report average enthalpy values of -6.0 kcal/mol for select solutes with supercritical carbon

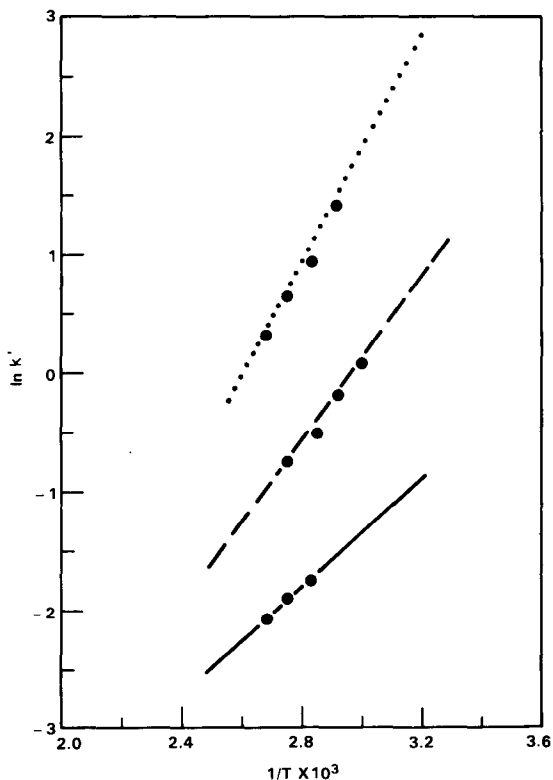


Fig. 2. Plots of $\ln k'$ versus $1/T$ for octadecane. Densities: —, 0.50 g/cm³; ---, 0.40 g/cm³; ·····, 0.30 g/cm³. The stationary phase is SE-54.

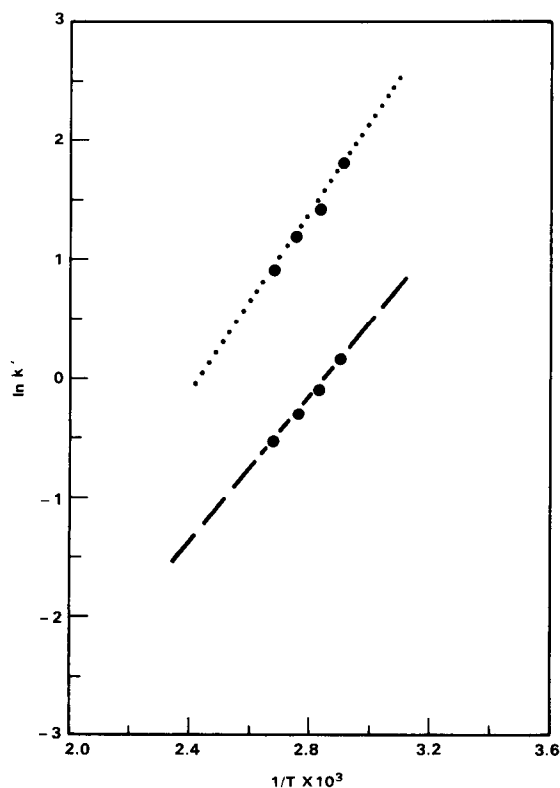


Fig. 3. Plots of $\ln k'$ versus $1/T$ for octadecanol. Densities: ---, 0.40 g/cm^3 ;, 0.30 g/cm^3 . The stationary phase is SE-54.

dioxide and nitrous oxide at a density of 0.80 g/cm^3 using a PRP-1 column (styrene-divinylbenzene copolymer). In reversed-phase liquid chromatography, Grushka *et al.*¹⁹ have reported values ranging from -2.0 to -6.0 kcal/mol , while Knox and Vasvari²⁰ have reported a wider range of enthalpies from -0.9 to -5.9 kcal/mol on permaphase-ODS with methanol-water (40:60) as the mobile phase. Meyer *et al.*²¹ and Martire *et al.*^{22,23} have reported enthalpies for the *n*-alkanes; hexane, heptane, and octane of -6.8 to -9.1 kcal/mol on *n*-tetracosane as the stationary phase, over a temperature range of 76 – 88°C with gas chromatography.

Semonian and Rogers¹⁵ have reported the trend in ΔH_T^0 as a function of density with pentane as a carrier gas using a packed, chemically modified silica column. The pressure range in their study was subcritical with a maximum reduced pressure of 0.61 being attained, while reduced temperature ranged from 0.95 to 1.05 . The general trend of ΔH_T^0 in their study was as the mobile phase density increases the enthalpy of solute transfer decreased for all the solutes studied. This trend is also reflected with SFC as seen in Tables I and II.

As the number of solute-solvent interactions increases with density the retention mechanism changes, which is reflected in the change of ΔH_T^0 with density. As density decreases one approaches the limiting case of gas chromatography, solute-

TABLE I

ENTHALPY OF TRANSFER (ΔH_T^0) FOR *n*-ALKANES AND *n*-ALKANOLS

Stationary phase, SE-54; fluid, carbon dioxide.

Density (g/cm ³)	ΔH_T^0 (kcal/mol)					
	Heptadecane	Octadecane	Nonadecane	Pentadecanol	Hexadecanol	Octadecanol
0.50	-3.9	-4.2	-4.3			
0.40	-6.5	-6.8	-7.1	-5.3	-5.6	-6.0
0.30	-8.6	-8.9	-9.4	-6.7	-6.9	-7.3

solvent interactions decrease and stationary phase-solute interactions dominate the retention process. The limiting case of liquid-like behavior is reached for fluids at high densities. In this case, the ΔH_T^0 values approach those for liquid chromatography where the solute-solvent interactions are prevalent. The region of moderate densities addressed through SFC in this work shows that density has an impact on the enthalpy of solute transfer.

Tables III and IV give ΔS_T^0 values for the solutes calculated using eqn. 6. The phase ratio of the columns were based on the film thickness of the stationary phase and the total column volume. Solvent swelling of the stationary phase as a function of pressure or temperature may impact these ΔS_T^0 values, but work by Sie *et al.*²⁴ and in this laboratory indicate that this contribution can be small for these solvent and stationary phase combinations. Therefore the phase ratio (ϕ) was assumed independent of density for the calculation of ΔS_T^0 . For the *n*-alkanols on SE-54 the entropy remains constant with density. With the *n*-alkanes on SE-54, the entropy becomes more negative as the density decreased. This trend is again similar to the earlier results of Semonian and Rogers¹⁵ with subcritical pentane. The entropy for the *n*-alkanes on OV-17 follow a different trend with density. A possible explanation could be due to the impact of solvation on the entropy of solute transfer between the mobile and stationary phase. A partition-like retention process for SE-54 may be inferred from the less negative ΔH_T^0 values between the two stationary phases at a

TABLE II

ENTHALPY OF TRANSFER (ΔH_T^0) FOR *n*-ALKANES

Stationary phase, OV-17; fluid, carbon dioxide.

Density (g/cm ³)	ΔH_T^0 (kcal/mol)		
	Heptadecane	Octadecane	Nonadecane
0.50	-5.9	-6.5	-6.3
0.38	-6.0	-6.2	-6.4
0.30	-6.7	-7.0	-7.3
0.20	-8.4	-8.9	-9.1

TABLE III

ENTROPY OF TRANSFER (ΔS_T^0) FOR *n*-ALKANES AND *n*-ALKANOLS

Stationary phase, SE-54; fluid, carbon dioxide. The phase ratio was assumed to be independent of density.

Density (g/cm ³)	ΔS_T^0 (cal/mol K)					
	Heptadecane	Octadecane	Nonadecane	Pentadecanol	Hexadecanol	Octadecanol
0.50	-7.1	-7.5	-7.4			
0.40	-12.1	-12.4	-12.7	-8.6	-9.1	-9.4
0.30	-15.2	-15.5	-16.2	-9.8	-9.8	-9.9

TABLE IV

ENTROPY OF TRANSFER (ΔS_T^0) FOR *n*-ALKANES

Stationary phase, OV-17; fluid, carbon dioxide. The phase ratio was assumed to be independent of density.

Density (g/cm ³)	ΔS_T^0 (cal/mol K)		
	Heptadecane	Octadecane	Nonadecane
0.50	-15.5	-17.0	-16.0
0.38	-12.5	-12.6	-12.7
0.30	-12.2	-12.5	-12.8
0.20	-14.0	-14.5	-14.6

density of 0.50 g/cm³. Therefore with OV-17, the entropy of solute transfer appears governed by an adsorption-like retention mechanism contributing to the trend seen in Table IV.

CONCLUSION

As mobile phase density of a supercritical fluid increases, the enthalpy of solute transfer (ΔH_T^0) is seen to decrease. This is most likely caused by the increased solute-solvent interactions which occur as fluid density increases. The enthalpy values reported here fall between those reported in the literature for liquid and gas chromatography with SFC approaching the gas chromatographic values at low densities and liquid chromatographic values at high densities.

The present results show a significant contrast between the SE-54 and more polar OV-17 stationary phase. The entropy of solute transfer (ΔS_T^0) suggests a dependence on the extent of stationary phase solvation by the supercritical fluid. However, more experimental work involving supercritical fluid solvation of these cross-linked stationary phases is needed to clarify our understanding of these phenomena.

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