An Examination of Factors Influencing the Thermodynamics of Correlation-Gas Chromatography as Applied to Large Molecules and Chiral Separations

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The effects of temperature and flow rate on enthalpies of transfer and the resulting vaporization enthalpies measured by correlation-gas chromatography are examined at the mean temperatures of measurement for a series of alkanes. The study is an effort to understand the parameters affecting the magnitude of the enthalpy of transfer of the analyte from the stationary phase of the column to the gas phase. An endothermic enthalpy of solution or association of the analyte with the stationary phase of the column, $\Delta_{\mathrm{sln}}H_{\mathrm{m}}(T_{\mathrm{m}})$, is observed which appears quite sensitive to temperature. A considerably less endothermic $\Delta_{\mathrm{sln}}H_{\mathrm{m}}(T_{\mathrm{m}})$ value is observed with (D)- and (L)-menthol, and this becomes weakly exothermic with (D)- and (L)-limonene on chiral columns containing cyclodextrin and its derivatives. The endothermicity and sensitivity to temperature observed on achiral columns offers an explanation of how it is possible to measure enthalpies of vaporization of large hydrocarbons that exceed the strength of the weakest bond in the molecule.

Introduction

Correlation-gas chromatography is proving to be a useful technique for the reliable evaluation of vaporization enthalpies and liquid phase vapor pressures of materials that are either solid or liquid at the temperatures of interest.[1−15] This technique does not measure vaporization enthalpies directly but rather correlates enthalpies of transfer from the stationary phase of the column to the vapor as measured by gas chromatography to the vaporization enthalpy of standards at the temperature of interest. The vaporization of the target molecules is evaluated from the correlation equation. It is an indirect means of obtaining vaporization enthalpies and liquid vapor pressures of materials at $T = 298.15$ K that are either solids or liquids at this temperature. As such, it has proven useful in validating thermochemical cycles involving sublimation, fusion, and vaporization enthalpies.[10,16] The technique is also capable of providing pure component vaporization enthalpies of materials that exist as mixtures[11−13] and of measuring the vaporization enthalpies of complex mixtures of hydrocarbons.[14,15] This article examines the thermodynamic relationship between the enthalpy of transfer from the stationary phase of the column to the vapor, $\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}(T_{\mathrm{m}})$, and vaporization enthalpy, $\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(T_{\mathrm{m}})$, of a series of analytes as a function of flow rate, temperature, and stationary phase.

A logarithmic relationship has been shown to exist between a compound's peak retention volume and its vapor pressure.[17] Peacock and Fuchs measured the temperature dependence of retention volume (V_{g}) and related the slope of the line obtained from a plot of $\ln(V_{\mathrm{g}})$ versus $(1/T)$ to the enthalpy of transfer of the solute from the stationary phase of the column to the gas phase divided by R where R is the gas constant.[18,19] The retention volume is dependent on a number of parameters including the carrier flow rate, the amount of stationary phase, the pressure differential, and a compressibility factor. These parameters are generally maintained relatively constant during an isothermal run. They are characterized by the constant C in eq 1.

$$V_{\mathrm{g}} = C(t - t_{\mathrm{nrr}}) = Ct_{\mathrm{a}} \tag{1}$$

The term t_{nrr} refers to the retention time of a nonretained reference compound, often the solvent or a substance such as methane that is not retained by the stationary phase at the temperature of measurement, and t refers to the observed retention time of a given analyte. A plot of $\ln(t_{\mathrm{a}}/t_{\mathrm{o}})$, where t_{a} is the adjusted retention time and t_{o} is the reference time, 1 min, vs $1/T$ results in a slope that is identical to the value obtained by using V_{g} and an intercept which remains proportional to the compound's vapor pressure off the column. Additionally, Peacock and Fuchs related the enthalpy of transfer of the solute from the stationary phase of the column, $\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}(T_{\mathrm{m}})$, to a sum of the vaporization enthalpy, $\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(T_{\mathrm{m}})$, and the enthalpy of solution of the solute, in the stationary phase, $\Delta_{\mathrm{sln}}H_{\mathrm{m}}(T_{\mathrm{m}})$, eq 2.

$$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}(T_{\mathrm{m}}) = \Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(T_{\mathrm{m}}) + \Delta_{\mathrm{sln}}H_{\mathrm{m}}(T_{\mathrm{m}}) \tag{2}$$

Peacock and Fuchs' chromatographic experiments and solution studies were conducted on packed columns using DC-200 silicone fluid. Since the gas chromatographic experiments were not conducted at the same temperature as the solution studies, $\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}(T_{\mathrm{m}})$ values were adjusted to $T = 298.15$ K from the mean temperature of measurement using estimated heat capacity values. Peacock and Fuchs found that the vaporization enthalpies calculated using eq 2 were not exactly equal to the literature values measured by other means but nearly so. Their values were related to the literature values by the following relationship[18]

$$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(298.15\ \mathrm{K})_{\mathrm{lit}} = 0.9696\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(298.15\ \mathrm{K})_{\mathrm{gc}} + 0.8374; \quad r^2 = 0.9999 \tag{3}$$

Although they do not comment on possible reasons for the slight differences observed, several possibilities come to mind. These include the approximate nature of the heat capacity corrections,

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10.1021/je900422c CCC: $40.75

Table 1. (A) Parameters of the Cox Equation (Equation 4),[a] (B) Parameters of the Third-Order Polynomial Used in the Calculations (Equation 5),[c] (C) Parameters of the Wagner Equation (Equation 6),[d] and (D) Coefficients of Equation 7:[e] $T/\mathrm{K}\cdot\log_{10}(p/p_o) = a_o/2 + \sum_{s=1}^{3} a_s E_s(x)$

(A)	T_b/K	A_o	$(10^3A_1)/(T/\mathrm{K})$	$(10^6A_2)/(T/\mathrm{K})^2$
decane	447.269	2.9669	−1.932579	1.64463
tetradecane	526.691	3.13624	−2.063853	1.54151
pentadecane	543.797	3.16774	−2.062348	1.48726
hexadecane	559.978	3.18271	−2.002545	1.38448
heptadecane	575.375	3.21826	−2.00254	1.38
octadecane	590.023	3.24741	−2.048039	1.36245
nonadecane	603.989	3.27626	−2.06271	1.35
eicosane	617.415	3.31181	−2.09536	1.34878
acenaphthene[b]	366.535	3.246001	−0.873359	0.53659254
quinoline[21]	510.298	2.85461	−1.30236	0.93118
isoquinoline[21]	516.391	2.85183	−1.26768	0.88569
7,8-benzoquinoline[22]	614.49	2.88454	−1.11802	0.66824
acridine[22]	618.059	2.89594	−1.11538	0.6486

(B)	$10^{-8}A/(T/\mathrm{K})^3$	$10^{-6}B/(T/\mathrm{K})^2$	$C/(T/\mathrm{K})$	D
heneicosane	1.9989	−2.9075	−98.135	6.6591
docosane	2.1713	−3.1176	110.72	6.5353
tricosane	2.3386	−3.322	310.77	6.4198
tetracosane	2.5072	−3.5286	530.15	6.2817
pentacosane	2.6738	−3.7307	741.19	6.1496
fluorene[10]	2.819123	−3.03948	2358.69	3.348

(C)	A_W	B_W	C_W	D_W	T_c/K	p_c/kPa	ref
naphthalene	−7.79639	2.25115	2.7033	−3.2266	748.4	4105	23
diphenylmethane	−9.023973	3.839191	−4.94231	−3.42478	778	3280	24
1-hexanol	−10.738	8.9016	−15.725	4.07	610.3	3417	25
(+)-limonene	−8.01789	2.15918	−3.20846	−3.53487	655	2900	26
quinaldine	−8.370206	2.914441	−3.761685	−3.195981	778	4030	36
2,6-dimethylquinoline	−8.993312	3.594873	−4.63173	−2.907492	786	3480	37

(D)	T_{min}/K	T_{max}/K	a_o	a_1	a_2	a_3
			experimental values			
1-octanol	386	480	1311.759	378.722	−8.221	0.443
1-decanol	400	529	1387.15	512.274	−13.792	1.418
			correlated values			
1-heptanol	343	518	1450.65	700.19	−26.29	2.45
1-undecanol	394	601	1678.92	806.60	−27.39	5.72

[a] From ref 20 unless noted otherwise. [b] Reference 27. The value in column 2 represents an arbitrary chosen reference temperature corresponding to the vapor pressure, p_o, of 198.0 Pa for acenaphthene in eq 6. [c] From ref 9 unless noted otherwise. [d] $T_r = T/T_c$. [e] From Ambrose et al.;[28] $E_s(x)$ is the Chebyshev Polynomial: $a_1(x) + a_2(2x^2 - 1) + a_3(4x^2 - 3x)$, $x = [2(T/\mathrm{K}) - (T_{max} + T_{min})/\mathrm{K}]/(T_{max} - T_{min})/\mathrm{K}$ and $p_o = 1$ kPa.

the possibility that the interactions of the solute on the stationary phase on the column is not truly a solution phenomena, and differences in the activity of the solute on the column and in solution due to concentration effects. An additional possibility concerns the dynamic nature of the measurement. Since the measurement of retention volume depends on flow rate, the relationship between retention volume and vapor pressure may have a kinetic component.

One aim of this article is to examine the role that flow rate, analyte, and the stationary phase play on the magnitude of $\Delta_{sln}{}^{g}H_m(T_m)$. New measurements to determine the role of flow rate on the magnitude under typical experimental conditions are reported. Additional impetus for this study arose in an effort to understand how it was possible to evaluate the vaporization enthalpies of large hydrocarbons whose vaporization enthalpies exceed the magnitude of the C−C bond strength given the very low vapor pressures expected of these molecules.[3] The vaporization enthalpies and vapor pressures of the even alkanes, tetraheptacosane, C_{74}, to dononacosane, C_{92}, admittedly by an extrapolative procedure, were evaluated at $T = 298.15$ K as ranging from (356 to 425) kJ·mol^{-1} and ($3\cdot10^{-27}$ to $1\cdot10^{-33}$) Pa, respectively. The vaporization enthalpies are in large excess of the 350 kJ·mol^{-1} normally assigned to the carbon−carbon bond strength, and the vapor pressures are considerably smaller than is currently feasible to measure by conventional techniques.

A series of experiments previously reported using analytes with well-documented thermochemical properties have been used to evaluate the relationship between $\Delta_{sln}{}^{g}H_m(T_m)$ and $\Delta_{l}{}^{g}H_m(T_m)$ as a function of temperature. These *n*-alkanes were chosen because of their ideal behavior and the fact that their vapor pressures and vaporization enthalpies as a function of temperature are well documented. Finally, in an effort to understand how the nature of the analyte affects $\Delta_{sln}{}^{g}H_m(T_m)$, the thermodynamics of a series of analytes with different functional groups including two chiral systems have also been examined. In all these cases, analytes were chosen in cases where reliable vapor pressures at the experimental temperatures of measurement are available.

The vapor pressures and vaporization enthalpies of all the analytes used in this study were either recommended values or calculated using vapor pressures obtained from the recommended constants of the Cox equation,[20] eq 4, the third-order polynomial,[9] eq 5, the Wagner equation,[23−26] eq 6, a relationship using the Chebyshev polynomial,[28] eq 7, and the Antoine equation,[29] eq 8.

$$\ln(p/p_o) = (1 - T_b/T)\exp(A_o + A_1(T/\mathrm{K}) + A_2(T/\mathrm{K})^2) \tag{4}$$

$$\ln(p/p_o) = A(T/\mathrm{K})^{-3} + B(T/\mathrm{K})^{-2} + C(T/\mathrm{K})^{-1} + D \tag{5}$$

$$\ln(p/p_c) = (1/T_r)[A_W(1 - T_r) + B_W(1 - T_r)^{1.5} + C_W(1 - T_r)^{2.5} + D_W(1 - T_r)^5] \tag{6}$$

$$(T/\mathrm{K})\cdot\log_{10}(p/p_o) = a_o/2 + \sum_{s=1}^{3} a_s E_s(x) \tag{7}$$

$$\log(p/p_o) = A - B/(T/\mathrm{K} + C) \tag{8}$$

Constants and definitions of all the terms in eqs 4 to 8 are provided in Tables 1A to 1D,[20−28] in the corresponding footnotes, and in ref 29; p_o is equal to 101.325 kPa. It should also be pointed out that the vapor pressures and vaporization enthalpies derived from eq 5 for henicosane to pentacosane were derived by extrapolation using correlation gas chromatography.[9] Recently, vapor pressures between T = (350 and 460) K have been reported for henicosane, tricosane, and pentacosane using a static device.[30] Experimental vapor pressures and those calculated using eq 5 in this temperature range are in good agreement. The vaporization enthalpies for all the analytes discussed in this article at temperatures other than T = 298.15 K were calculated from vapor pressures using these equations at the same temperatures as the gas chromatographic studies.

Experimental Section

All the *n*-alkanes examined, tetradecane, pentadecane, hexadecane, octadecane, nonadecane, and eicosane, were commercial samples purchased from Aldrich. (DL)-Limonene was prepared by mixing (D)-limonene (97 %) and (L)-limonene (96 %) purchased from the same supplier. (L)-Menthol (USP) and (DL)-menthol (Practical grade) were obtained from Cameron and Stuart, Inc. and Eastman, respectively. The composition of the *n*-alkanes has been described previously.[9] Correlation gas chromatography experiments were performed on several different HP 5890 Gas Chromatographs, each equipped with a split/splitless capillary injection port and a flame ionization detector and run at split ratios of approximately 50/1 to 100/1. Retention times were recorded to three significant figures following the decimal point using either an HP 3396 Series III integrator or an HP Chemstation. The compounds were run isothermally on a 30 m, 0.25 mm ID, Supelco SPB-5 column, a 30 m, 0.25 mm ID J&W DB5-MS column, and a 30 m, 0.53 mm ID Restek RTX-5. Some of these experiments, Tables 5 to 7, have been performed and reported previously. While the suppliers of the columns are different, all columns except where noted have similar (5 % phenyl)methylsiloxane stationary phases. Experiments with the chiral substrates, (L)-limonene and (D)-menthol, were performed on both chiral and achiral columns. The achiral column used was a 30 m, 0.53 mm ID, 3 μm bonded phase, Rtx-1301 column consisting of crossbonded 6 % cyanopropylphenyl-/94 % dimethylpolysiloxane. Experiments with (DL)-

Table 2. Enthalpies of Transfer and Vaporization Enthalpies at a Flow Rate of (A) 0.67 mL·min^{-1} on a 0.25 mm ID DB-5MS Column (15 PSI), (B) 0.45 mL·min^{-1} on a 0.25 mm ID DB-5MS Column (10 PSI), and (C) 0.27 mL·min^{-1} on a 0.25 mm ID DB-5MS Column (6 PSI)

(A)	−slope		$\Delta_{\mathrm{sln}}^{\mathrm{g}}H_m$(448 K)	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_m$(298.15 K)(lit)	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_m$(298.15 K)(calc)
run 1	(T/K)	intercept	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}
tetradecane	6213.6	13.217	51.66	71.73	71.7 ± 0.8
pentadecane	6670.8	13.793	55.46	76.77	76.7 ± 0.9
hexadecane	7120.3	14.356	59.20	81.35	81.6 ± 0.9
heptadecane	7550.2	14.879	62.77	86.47	86.3 ± 1.0
octadecane	8012.8	15.476	66.62	91.44	91.4 ± 1.0

$$\Delta_1^{\mathrm{g}}H_m(298.15\ \mathrm{K})/\mathrm{kJ\cdot mol^{-1}} = (1.319 \pm 0.016)\Delta_{\mathrm{sln}}^{\mathrm{g}}H_m(448\ \mathrm{K}) - (3.53 \pm 0.18) \qquad r^2 = 0.9996 \tag{9}$$

(B)	−slope		$\Delta_{\mathrm{sln}}^{\mathrm{g}}H_m$(448 K)	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_m$(298.15 K)(lit)	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_m$(298.15 K)(calc)
run	(T/K)	intercept	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}
tetradecane	6207.4	12.82	51.61	71.73	71.7 ± 0.7
pentadecane	6648.0	13.358	55.27	76.77	76.6 ± 0.7
hexadecane	7092.3	13.908	58.96	81.35	81.6 ± 0.8
heptadecane	7529.6	14.448	62.60	86.47	86.4 ± 0.8
octadecane	7982.6	15.023	66.36	91.44	91.4 ± 0.9

$$\Delta_1^{\mathrm{g}}H_m(298.15\ \mathrm{K})/\mathrm{kJ\cdot mol^{-1}} = (1.333 \pm 0.013)\Delta_{\mathrm{sln}}^{\mathrm{g}}H_m(448\ \mathrm{K}) - (2.95 \pm 0.15) \qquad R^2 = 0.9997 \tag{10}$$

(C)	−slope		$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}\mathrm{H}_m$(448 K)	$\Delta_{\mathrm{l}}{}^{\mathrm{g}}\mathrm{H}_m$(298.15 K)(lit)	$\Delta_{\mathrm{l}}^{\mathrm{g}}\mathrm{H}_m$(298.15 K)(calc)
run 3	(T/K)	intercept	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}
tetradecane	6187.4	12.274	51.44	71.73	71.7 ± 0.7
pentadecane	6628.4	12.812	55.11	76.77	76.6 ± 0.7
hexadecane	7074.2	13.365	58.81	81.35	81.6 ± 0.8
heptadecane	7512.6	13.907	62.46	86.47	86.4 ± 0.8
octadecane	7959.3	14.468	66.17	91.44	91.4 ± 0.9

$$\Delta_1^{\mathrm{g}}H_m(298.15\ \mathrm{K})/\mathrm{kJ\cdot mol^{-1}} = (1.334 \pm 0.0134)\Delta_{\mathrm{sln}}^{\mathrm{g}}H_m(448\ \mathrm{K}) - (3.101 \pm 0.156) \qquad R^2 = 0.9997 \tag{11}$$

Table 3. Enthalpies of Transfer and Vaporization Enthalpies (kJ·mol^{-1}) at (A) 2.29 mL·min^{-1} on a 0.53 mmID RTX-5 Column (2PSI), (B) 5.67 mL·min^{-1} on a 0.53 mmID RTX-5 Column (5PSI), (C) 12.3 mL·min^{-1} on a 0.53 mmID Rtx-5 Column (12PSI)

(A) run 4	−slope		$\Delta_{sln}{}^{g}H_m$(448 K)	$\Delta_{l}{}^{g}H_m$(298.15 K)(lit)	$\Delta_{l}{}^{g}H_m$(298.15 K)(calc)
2 PSI Rtx-5	(*T*/K)	intercept	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}
tetradecane	6126.8	12.102	50.94	71.73	71.8 ± 0.6
pentadecane	6543.4	12.596	54.40	76.77	76.8 ± 0.6
hexadecane	6962.3	13.101	57.88	81.35	81.1 ± 0.7
heptadecane	7386.5	13.622	61.41	86.47	85.9 ± 0.7
octadecane	7816.3	14.158	64.98	91.44	90.9 ± 0.7

$$\Delta_{1}{}^{g}H_m(298.15\ \text{K})/\text{kJ}\cdot\text{mol}^{-1} = (1.918 \pm 0.014)\Delta_{sln}{}^{g}H_m(448\ \text{K}) + (9.70 \pm 0.40) \qquad R^2 = 0.9996 \qquad (12)$$

(B) run 5	−slope		$\Delta_{sln}{}^{g}H_m$(448 K)	$\Delta_{l}{}^{g}H_m$(298.15 K)(lit)	$\Delta_{l}{}^{g}H_m$(298.15 K)(calc)
5 PSI Rts-5	(*T*/K)	intercept	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}
tetradecane	6170.6	12.206	51.30	71.73	71.8 ± 0.6
pentadecane	6590.1	12.707	54.79	76.77	76.6 ± 0.6
hexadecane	7011.9	13.219	58.29	81.35	81.5 ± 0.7
heptadecane	7439.2	13.747	61.85	86.47	86.4 ± 0.7
octadecane	7872.0	14.29	65.45	91.44	91.4 ± 0.7

$$\Delta_{1}{}^{g}H_m(298.15\ \text{K})/\text{kJ}\cdot\text{mol}^{-1} = (1.791 \pm 0.040)\Delta_{sln}{}^{g}H_m(448\ \text{K}) + (22.46 \pm 1.38) \qquad r^2 = 0.9971 \qquad (13)$$

(C) run 6	−slope		$\Delta_{sln}{}^{g}H_m$(448 K)	$\Delta_{l}{}^{g}H_m$(298.15 K)(lit)	$\Delta_{l}{}^{g}H_m$(298.15 K)(calc)
12 PSI RTX-5	(*T*/K)	intercept	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}
tetradecane	6162.8	13.795	51.24	71.73	71.8 ± 1.0
pentadecane	6576.3	14.284	54.67	76.77	76.6 ± 1.1
hexadecane	7000.3	14.801	58.20	81.35	81.5 ± 1.1
heptadecane	7419.6	15.312	61.68	86.47	86.4 ± 1.2
octadecane	7859.4	15.871	65.34	91.44	91.5 ± 1.3

$$\Delta_{1}{}^{g}H_m(298.15\ \text{K})/\text{kJ}\cdot\text{mol}^{-1} = (2.031 \pm 0.012)\Delta_{sln}{}^{g}H_m(448\ \text{K}) + (2.352 \pm 0.38) \qquad r^2 = 0.9998 \qquad (14)$$

Table 4. Summary of the Effect of Flow Rate on $\Delta_{sln}{}^{g}H_m$(448 K)

	flow rate	$\Delta_{sln}{}^{g}H_m$(448 K)/kJ·mol^{-1}				
column	mL·min^{-1}	tetradecane	pentadecane	hexadecane	heptadecane	octadecane
Rtx-5						
	12.3	51.24	54.67	58.20	61.68	65.34
	5.7	51.30	54.79	58.29	61.85	65.44
	2.3	50.94	54.4	57.88	61.41	64.98
	0	50.99 ± 0.23	54.48 ± 0.26	57.95 ± 0.27	61.51 ± 0.31	65.06 ± 0.30
DB5-MS						
	0.67	51.66	55.46	59.2	62.77	66.62
	0.45	51.61	55.27	58.96	62.6	66.36
	0.27	51.44	55.11	58.81	62.46	66.17
	0	51.32 ± 0.1	54.87 ± 0.004	58.54 ± 0.04	62.25 ± 0.01	65.86 ± 0.02

limonene on the chiral column were performed on an 30 m, 0.25 mm ID, 25 μm bonded phase, Restek Rt-βDEXcst column, which consists of β-cyclodextrin doped into 14 % cyanopropylphenyl-/86 % dimethylpolysiloxane. Experiments with (DL)-menthol were performed on a chiral 30 m, 0.25 mm ID, 25 μm nonbonded phase, Rt-βDEXm column consisting of permethylated β-cyclodextrin also doped into 14 % cyanopropylphenyl-/86 % dimethylpolysiloxane. The injection and detector temperatures were maintained at different temperatures but at least 10 K above the highest temperature of a series of runs. Helium was used as the carrier gas. Methane or the solvent was used as the nonretained reference. Adjusted retention times, t_a, were calculated by subtracting the measured retention time of the solvent from the retention time of each analyte as a function of temperature over a 30 K range at 5 K intervals. Column temperatures were controlled by the gas chromatograph and were monitored independently by using a Fluke digital thermometer. Temperature was maintained constant by the gas chromatograph to ± 0.1 K. All plots of ln(t_o/t_a), vs 1/T, where t_o = 1 min, were characterized with correlation coefficients, r^2, > 0.99. The retention times measured for all analytes are reported as Supporting Information either associated with this article or with articles published previously.

Results

The retention volume of an analyte on a specific column and at a specific temperature is primarily determined by head pressure, column diameter, and column length. Typical head pressures used with capillary columns range from 2 to 15 pounds·in^{-2}. Enthalpies of transfer from the stationary phase to the gas phase in our work have usually been measured within this range and on capillary columns with diameters between 0.25 mm and 0.53 mm. The effect of flow rate on the magnitude of $\Delta_{sln}{}^{g}H_m$(448 K) was evaluated using a series of n-alkanes from tetradecane to octadecane on two 30 m columns, a 0.25

Table 5. Values of (A) $\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(449 K) and $\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(449 K), (B) $\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(509 K) and $\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(509 K), and (C) $\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(539 K) and $\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(539 K) on an SPB-5 Column

	−slope		$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(449 K)	$(\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(449\ \mathrm{K}))/\mathrm{kJ\cdot mol^{-1}}$		$(\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(298\ \mathrm{K}))/\mathrm{kJ\cdot mol^{-1}}$	
(A)	*T*	intercept	$\mathrm{kJ\cdot mol^{-1}}$	(lit)[20]	calcd	(lit)[20]	(calc)[9]
tetradecane	6393.8 ± 95	14.161 ± 0.01	53.2 ± 0.8	56.92	57.0 ± 0.8	71.7	71.8 ± 1.0
pentadecane	6787.9 ± 73	14.597 ± 0.01	56.4 ± 0.6	60.71	60.6 ± 0.8	76.8	76.5 ± 1.0
hexadecane	7251.5 ± 62	15.190 ± 0.01	60.3 ± 0.5	64.50	64.8 ± 0.9	81.4	82.0 ± 1.1
heptadecane	7612.6 ± 65	15.587 ± 0.01	63.3 ± 0.5	68.19	68.1 ± 0.9	86.5	86.3 ± 1.2
octadecane	8014.8 ± 71	16.070 ± 0.01	66.6 ± 0.6	72.11	71.8 ± 1.0	91.4	91.1 ± 1.3
nonadecane	8457.4 ± 74	16.640 ± 0.01	70.3 ± 0.6	76.01	75.8 ± 1.0	96.4	96.4 ± 1.4
eicosane	8919.6 ± 85	17.257 ± 0.01	74.2 ± 0.7	79.81	80.1 ± 1.1	101.8	101.9 ± 1.4

$$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(449\ \mathrm{K})/\mathrm{kJ\cdot mol^{-1}} = (1.098 \pm 0.0133)\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}(449\ \mathrm{K}) - (1.39 \pm 0.25) \qquad r^2 = 0.9993 \tag{15}$$

$$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(298\ \mathrm{K})/\mathrm{kJ\cdot mol^{-1}} = (1.436 \pm 0.019)\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}(449\ \mathrm{K}) + (4.54 \pm 0.35) \qquad r^2 = 0.9991 \tag{16}$$

	−slope		$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(509 K)	$(\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(509\ \mathrm{K}))/\mathrm{kJ\cdot mol^{-1}}$		$(\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(298\ \mathrm{K}))/\mathrm{kJ\cdot mol^{-1}}$	
(B)	*T*	intercept	$\mathrm{kJ\cdot mol^{-1}}$	(lit)	calcd	(lit)[20]	(calc)[9]
heptadecane	6108.2 ± 78.2	12.148 ± 0.008	50.8 ± 0.7	62.83[20]	62.9 ± 0.3	86.5	86.4 ± 2.0
octadecane	6489.9 ± 63.8	12.584 ± 0.006	54.0 ± 0.5	66.34[20]	66.2 ± 0.3	91.4	91.4 ± 2.2
nonadecane	6901.0 ± 58.7	13.077 ± 0.006	57.4 ± 0.5	69.74[20]	69.8 ± 0.3	96.4	96.7 ± 2.3
eicosane	7270.0 ± 60.5	13.496 ± 0.006	60.4 ± 0.5	73.07[20]	73.1 ± 0.3	101.8	101.6 ± 2.4
heneicosane	7670.9 ± 65.3	13.974 ± 0.006	63.8 ± 0.5	76.66[9]	76.6 ± 0.3		106.8 ± 2.5
docosane	8064.5 ± 71.6	14.439 ± 0.007	67.1 ± 0.6	80.13[9]	80.1 ± 0.4		111.9 ± 2.7
tricosane	8451.1 ± 73.9	14.897 ± 0.008	70.3 ± 0.7	83.54[9]	83.5 ± 0.4		117.0 ± 2.8

$$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(509\ \mathrm{K})/\mathrm{kJ\cdot mol^{-1}} = (1.062 \pm 0.004)\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}(509\ \mathrm{K}) + (8.94.02 \pm 0.07) \qquad r^2 = 0.9999 \tag{17}$$

$$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(298\ \mathrm{K})/\mathrm{kJ\cdot mol^{-1}} = (1.57 \pm 0.04)\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}(509\ \mathrm{K}) + (6.66 \pm 0.30)^{9} \qquad r^2 = 0.9985 \tag{18}$$

	−slope		$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(539 K)	$(\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(539\ \mathrm{K}))/\mathrm{kJ\cdot mol^{-1}}$		$(\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(298\ \mathrm{K}))/\mathrm{kJ\cdot mol^{-1}}$	
(C)	*T*	intercept	$\mathrm{kJ\cdot mol^{-1}}$	(lit)	calcd	(lit)[20]	(calc)[9]
nonadecane	6165.3 ± 125	11.692 ± 0.01	51.3 ± 1.1	67.08[20]	67.2 ± 0.5	96.4[20]	96.8 ± 2.2
eicosane	6483.0 ± 128	12.013 ± 0.01	53.9 ± 1.1	70.15[20]	70.0 ± 0.5	101.8[20]	101.8 ± 2.3
heneicosane	6888.5 ± 128	12.487 ± 0.01	57.3 ± 1.1	73.41[9]	73.5 ± 0.5	106.8[9]	106.8 ± 2.5
docosane	7256.5 ± 121	12.906 ± 0.01	60.3 ± 1.0	76.68[9]	76.7 ± 0.5	111.9[9]	112.0 ± 2.5
tricosane	7619.9 ± 116	13.318 ± 0.01	63.4 ± 1.0	79.89[9]	79.9 ± 0.5	117.0[9]	117.0 ± 2.7
tetracosane	7972.5 ± 113	13.713 ± 0.01	66.3 ± 0.9	83.0[9]	83.0 ± 0.6		121.9 ± 2.8
pentacosane	8320.7 ± 112	14.105 ± 0.01	69.2 ± 0.9	86.05[9]	86.0 ± 0.6		126.8 ± 2.9

$$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(539\ \mathrm{K})/\mathrm{kJ\cdot mol^{-1}} = (1.053 \pm 0.007)\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}(539\ \mathrm{K}) + (13.20 \pm 0.106) \qquad r^2 = 0.9998 \tag{19}$$

$$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(298\ \mathrm{K})/\mathrm{kJ\cdot mol^{-1}} = (1.67 \pm 0.042)\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}(539\ \mathrm{K}) + (11.04 \pm 0.41) \qquad r^2 = 0.9985 \tag{20}$$

mm diameter J & W DB5-MS, and a 0.53 mm diameter Restek RTX-5 capillary column and the resulting values of $\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(448 K) extrapolated to a zero flow rate. Retention times are available in the Supporting Information. Flow rates were calculated using the retention time of the nonretained reference, the column diameter, and the nominal column length. The flow rates varied from (0.27 to 0.67) $\mathrm{mL\cdot min^{-1}}$ (DB5-MS column) and from (2.29 to 12.3) $\mathrm{mL\cdot min^{-1}}$ (RTX-5 column). Peak shapes were Gaussian on the RTX-5 column at all head pressures, but a slight distortion was observed on the DB5-MS column at (10 and 15) psi. The peaks at these head pressures appeared to approximate a right triangle with a positive slope. Both columns have similar stationary phases, as described in the Experimental Section. Tables 2A to 2C and 3A to 3C summarize the results of two sets of three experiments run under these conditions. The vaporization enthalpies at $T = 298.15$ K listed in column 5 of both these sets of tables are those recommended by Ruzicka and Majer.[20] The vaporization enthalpy values calculated using the equations obtained by correlation, eqs 9 to 14, shown at the bottom of each table and the results reported in the last two columns of the table demonstrate that the correlations remain quite linear, and the vaporization enthalpies of these *n*-alkanes are well reproduced at all these flow rates. Figure 1 illustrates how $\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(448 K) values obtained on the two columns vary with flow rate. The values appear to be decreasing slightly with decreasing flow rate. Results from the DB5-MS column appear to be most sensitive to flow rate, consistent with the peak shape observed. Extrapolating the results obtained on the Rtx-5 and DB5-MS columns to zero flow rate results in values that appear to be converging. The limiting values at zero flow are summarized in Table 4 for each of the *n*-alkanes on the two columns. The limiting values do not appear to be significantly different from the values obtained at higher flow rates, suggesting that the typical flow rates used in gas chromatography with capillary columns are not important parameters affecting the magnitude of $\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}(T_{\mathrm{m}})$ and have no effect on the resulting vaporization enthalpies obtained by correlation. However, the results suggest that measurements of $\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}(T_{\mathrm{m}})$ are not truly equilibrium measurements either. The uncertainties reported at zero flow were calculated from the uncertainties associated with the

Table 6. Values of $-\Delta_{sln}{}^{g}H_m(T)$, $-\Delta_{l}{}^{g}H_m(T)$, and $\Delta_{sln}H_m(T)$ as a Function of Temperature[a]

	$-\Delta_{sln}{}^{g}H_m$(449 K) kJ·mol^{-1}	$-\Delta_{l}{}^{g}H_m$(449 K) kJ·mol^{-1}(lit)	$\Delta_{sln}H_m$(449 K) kJ·mol^{-1}
tetradecane	−53.2 ± 0.8	−56.92	3.7 ± 0.8
pentadecane	−56.4 ± 0.6	−60.71	4.3 ± 0.6
hexadecane	−60.3 ± 0.5	−64.5	4.2 ± 0.5
heptadecane	−63.3 ± 0.5	−68.19	4.9 ± 0.5
octadecane	−66.6 ± 0.6	−72.11	5.5 ± 0.6
nonadecane	−70.3 ± 0.6	−76.01	5.7 ± 0.6
eicosane	−74.2 ± 0.7	−79.81	5.6 ± 0.7
	$-\Delta_{sln}{}^{g}H_m$(509 K) kJ·mol^{-1}	$-\Delta_{l}{}^{g}H_m$(509 K) kJ·mol^{-1}(lit)	$\Delta_{sln}H_m$(509 K) kJ·mol^{-1}
heptadecane	−50.8 ± 0.7	−62.83	12.0 ± 0.7
octadecane	−54.0 ± 0.5	−66.34	12.3 ± 0.5
nonadecane	−57.4 ± 0.5	−69.82	12.4 ± 0.5
eicosane	−60.4 ± 0.5	−73.07	12.7 ± 0.5
heneicosane	−63.8 ± 0.5	−76.66	12.9 ± 0.5
docosane	−67.1 ± 0.6	−80.13	13.0 ± 0.6
tricosane	−70.3 ± 0.7	−83.54	13.2 ± 0.7
	$-\Delta_{sln}{}^{g}H_m$(539 K) kJ·mol^{-1}	$-\Delta_{l}{}^{g}H_m$(539 K) kJ·mol^{-1}(lit)	$\Delta_{sln}H_m$(539 K) kJ·mol^{-1}
nonadecane	−51.3 ± 1.1	−67.17	15.9 ± 1.1
eicosane	−53.9 ± 1.1	−70.15	16.3 ± 1.1
heneicosane	−57.3 ± 1.1	−73.41	16.1 ± 1.1
docosane	−60.3 ± 1.0	−76.68	16.4 ± 1.0
tricosane	−63.4 ± 1.0	−79.89	16.5 ± 1.0
tetracosane	−66.3 ± 0.9	−83.00	16.7 ± 0.9
pentacosane	−69.2 ± 0.9	−86.05	16.9 ± 0.9

[a] Measured on a 30 m Supelco SPB-5 capillary column.[9]

intercept of the lines illustrated in Figure 1 obtained by a linear regression analysis.

The effect of temperature on the magnitude of $\Delta_{sln}{}^{g}H_m(T_m)$ is illustrated in Table 5A to 5C for a series of *n*-alkanes. The retention times and the resulting values of $\Delta_{sln}{}^{g}H_m(T_m)$ and $\Delta_{l}{}^{g}H_m$(298.15 K) have been reported previously.[9] In this article, the vaporization enthalpies of tetradecane to eicosane have been adjusted to the mean temperature of the gc measurements, $T =$ (449, 509, and 539) K, using the actual temperatures and temperature range employed in the gc experiments for the calculations. An examination of the correlation equations and their corresponding coefficients associated with eqs 15, 17, and 19 of Tables 5A to 5C suggests good linear relationships between $\Delta_{sln}{}^{g}H_m(T_m)$ and $\Delta_{l}{}^{g}H_m(T_m)$ at these temperatures as well as with $\Delta_{l}{}^{g}H_m$(298.15 K), eqs 16, 18, and 20.[9] Uncertainties in $\Delta_{sln}{}^{g}H_m(T_m)$ were calculated from the uncertainty associated with the slope of the $\ln(t_o/t_a)$ vs $(1/T)$ plot and the uncertainties in $\Delta_{l}{}^{g}H_m(T_m)$, from the uncertainties associated with the slopes and intercepts associated with the correlation equations, eqs 15 to 20. Applying eq 2 to these results allows an evaluation of the magnitude of interaction of each solute with the stationary phase of the column as a function of temperature, $\Delta_{sln}H_m(T_m)$. The resulting enthalpies of solution are summarized in Table 6. The results indicate that the enthalpy for the process of transferring the solute from the gas phase to the stationary phase of the column, $-\Delta_{sln}{}^{g}H_m(T_m)$, is less exothermic than the process of condensing the vapor, $-\Delta_{l}{}^{g}H_m(T_m)$. This implies that the enthalpy of interaction of the solute on the stationary phase of the column at the temperature of measurement is weaker than the interaction of the solute with itself, resulting in an endothermic enthalpy of solution. In turn, this reduces the enthalpy necessary to vaporize the solute off the column. In addition, this endothermic effect appears to be quite sensitive to temperature, increasing with increasing temperature. This is illustrated further in Figure 2 where $\Delta_{sln}H_m(T_m)$ from Table 6 is plotted against temperature for nonadecane and eicosane. Similar results are obtained for the other *n*-alkanes for which $\Delta_{sln}H_m(T_m)$ values are available at only two temperatures (not shown). The effect appears quite linear with temperature, and although curvature might be observed with data at additional temperatures, the results suggest that $\Delta_{sln}H_m(T_m)$ will become thermoneutral at approximately 400 K and perhaps exothermic at lower temperatures if the trend continues.

This endothermic effect is not limited to just the *n*-alkanes. Tables 7A to 7C summarize similar results reported previously for some aromatic hydrocarbons,[10] heterocyclic aromatic compounds,[1] and alcohols.[7] Correlation of $\Delta_{sln}{}^{g}H_m(T_m)$ with $\Delta_{l}{}^{g}H_m(T_m)$ at T_m is also quite linear as illustrated by comparison of the literature and calculated values of $\Delta_{l}{}^{g}H_m(T_m)$ in columns 5 and 6 of these tables and by the magnitude of correlation coefficients associated with eqs 21 to 23. Similar endothermic enthalpies of solution are calculated by eq 2 as reported in the last column of these tables. The enthalpies of solution appear to be more sensitive to the nature of the compound and/or experimental conditions and condition of the column than they do to the size of the analyte. The more polar compounds appear to have the most endothermic enthalpies of solution on (5 % phenyl)methylsiloxane stationary phases.

An additional study was conducted to examine the relationship between $\Delta_{sln}{}^{g}H_m(T_m)$ and $\Delta_{l}{}^{g}H_m(T_m)$ for (DL)-limonene and (DL)-menthol on both chiral and achiral columns. The thermodynamics associated with chiral separations of (DL)-limonene and (DL)-menthol have been previously studied.[31,32] To our knowledge, correlation-gas chromatography experiments have not been used previously to obtain thermochemical data on chiral separations. Two different chiral columns were used which differed in the composition of the chiral auxiliary. β-Cyclodextrin was used for resolving (DL)-limonene, and permethylated β-cyclodextrin was used for resolving (DL)-menthol. Both cyclodextrins were doped onto cyanopropylphenyl-dimethylsiloxane. The chemical makeup of the achiral column consisted only of cyanopropylphenyl-dimethylpolysiloxane but in a different ratio as noted in the Experimental Section. These experiments allow a rough comparison of the effect of the chiral auxiliary on both the magnitude of interaction with each of the two enantiomers and with the achiral materials used as standards.

The results using (DL)-limonene on an achiral column are summarized in Table 8 and those on the chiral column in Table 9. Table 8 summarizes the vaporization enthalpies obtained by correlation both at the mean temperature of the gc measurements, $T = 404$ K, and at $T = 298.15$ K. The enthalpies of transfer at $T = 404$ K correlate quite well with the vaporization enthalpies of the standards at $T = 298.15$ K. The vaporization enthalpy of (+)-limonene has previously been reported from vapor pressures measured using a twin ebulliometric apparatus.[26] A value of (49.59 ± 0.18) kJ·mol^{-1} was reported at $T = 298.15$ K, and this can be compared to a value of (49.8 ± 1.9) kJ·mol^{-1} calculated for the racemic mixture using correlation eq 24. In separate experiments, the vaporization enthalpies of the chiral and racemic forms measured by correlation gas chromatography on an achiral Rtx-5 column are also both found to be within experimental error, (50.5 ± 0.4) kJ·mol^{-1}.[33] The enthalpies of solution are all endothermic and show a slight increase with the size of the molecule, similar to what has been observed previously.

Different results are found for (DL)-limonene on the chiral column. These results are reported in Table 9. Good correlations between $\Delta_{sln}{}^{g}H_m(T)$ and $\Delta^{g}{}_{l}H_m(T)$ are observed on the chiral column

Table 7. Values of (A) $\Delta_{sln}{}^{g}H_m$(430 K) and $\Delta_{l}{}^{g}H_m$(430 K), (B) $\Delta_{sln}{}^{g}H_m$(440 K) and $\Delta_{l}{}^{g}H_m$(440 K), and (C) $\Delta_{sln}{}^{g}H_m$(402 K) and $\Delta_{l}{}^{g}H_m$(402 K) on an SPB-5 Column[a]

(A)	−slope		$\Delta_{sln}{}^{g}H_m$(430 K)	$\Delta_{l}{}^{g}H_m$(430 K)	$\Delta_{l}{}^{g}H_m$(430 K)	$\Delta_{sln}H_m$(430 K)[c]
T_m = 429.9 K	T	intercept	kJ·mol^{-1}	kJ·mol^{-1}(lit)[b]	kJ·mol^{-1}(calcd)	kJ·mol^{-1}
decane	4205.6	10.134	35.0 ± 0.1	43.06	44.3 ± 2.8	8.1 ± 0.1
naphthalene	4530.7	9.743	37.7 ± 0.1	47.63	47.1 ± 3.0	10.0 ± 0.1
diphenylmethane	5648.3	11.255	47.0 ± 0.2	56.75	56.7 ± 3.5	9.8 ± 0.2
acenaphthene	5610.2	10.899	46.6 ± 0.1	57.58	56.4 ± 3.6	10.9 ± 0.1
fluorene	5951.9	11.272	49.5 ± 0.2	59.94	59.4 ± 3.7	10.5 ± 0.2
hexadecane	6876.3	13.405	57.2 ± 0.2	66.31	67.4 ± 4.1	9.1 ± 0.2

$$\Delta_{l}{}^{g}H_m(430\ \text{K})/\text{kJ}\cdot\text{mol}^{-1} = (1.039 \pm 0.059)\Delta_{sln}{}^{g}H_m(430\ \text{K}) + (7.94 \pm 1.07) \qquad r^2 = 0.9872 \tag{21}$$

(B)	−slope		$\Delta_{sln}{}^{g}H_m$(440 K)	$\Delta_{l}{}^{g}H_m$(440 K)	$\Delta_{l}{}^{g}H_m$(440 K)	$\Delta_{sln}H_m$(440 K)[c]
T_m = 439.9 K	T	intercept	kJ·mol^{-1}	kJ·mol^{-1}(lit)[b]	kJ·mol^{-1}(calcd)	kJ·mol^{-1}
quinoline	4706.2	10.408	39.1 ± 0.4	50.99	50.8 ± 2.0	11.9 ± 0.4
isoquinoline	4766.5	10.444	39.6 ± 0.4	51.92	51.3 ± 2.0	12.3 ± 0.4
quinaldine	5034.7	10.866	41.9 ± 0.4	53.26	53.8 ± 2.1	11.4 ± 0.4
2,6-dimethylquinoline	5456.4	11.346	45.4 ± 0.5	57.16	57.7 ± 2.2	11.8 ± 0.5
7,8-benzoquinoline	6532.3	12.259	54.3 ± 0.5	67.55	67.8 ± 2.6	13.2 ± 0.5
acridine	6580.3	12.325	54.7 ± 0.5	68.72	68.2 ± 2.6	14.0 ± 0.5

$$\Delta_{l}{}^{g}H_m(440\ \text{K})/\text{kJ}\cdot\text{mol}^{-1} = (1.12 \pm 0.037)\Delta_{sln}{}^{g}H_m(440\ \text{K}) + (6.94 \pm 0.58) \qquad r^2 = 0.9956 \tag{22}$$

	−slope		$\Delta_{sln}{}^{g}H_m$(402 K)	$\Delta_{l}{}^{g}H_m$(402 K)	$\Delta_{l}{}^{g}H_m$(402 K)	$\Delta_{sln}H_m$(402 K)
(C)	T	intercept	kJ·mol^{-1}	kJ·mol^{-1}(lit)	kJ·mol^{-1}(calc)	kJ·mol^{-1}
1-hexanol	3971.6	10.983	33.0 ± 1.0	50.10	50.5 ± 1.4	17.1 ± 1.0
1-heptanol	4386.8	11.366	36.5 ± 0.6	54.36	54.1 ± 1.5	17.9 ± 0.6
1-octanol	4816.9	11.827	40.1 ± 0.6	58.03	57.8 ± 1.6	18.0 ± 0.6
1-decanol	5703	12.874	47.4 ± 0.5	65.50	65.3 ± 1.8	18.1 ± 0.5
1-undecanol	6206.4	13.571	51.6 ± 0.2	69.28	69.6 ± 1.9	17.7 ± 0.2

$$\Delta_{l}{}^{g}H_m{}^{o}(402\ \text{K})/\text{kJ}\cdot\text{mol}^{-1} = (1.025 \pm 0.027)\Delta_{sln}{}^{g}H_m{}^{o}(402\ \text{K}) + (16.68 \pm 0.41) \qquad r^2 = 0.9980 \tag{23}$$

[a] The retention times, slopes, and intercepts of the *n*-alkanes,[9] PAHs,[10] nitrogen heterocycles,[1] and 1-alkanols of this table have previously been reported. [b] Calculated at the mean temperatures indicated from the vapor pressures derived from the parameters given in Tables 1A to 1D. [c] $\Delta_{l}{}^{g}H_m$(402 K)(lit) − $\Delta_{sln}{}^{g}H_m$(402 K).

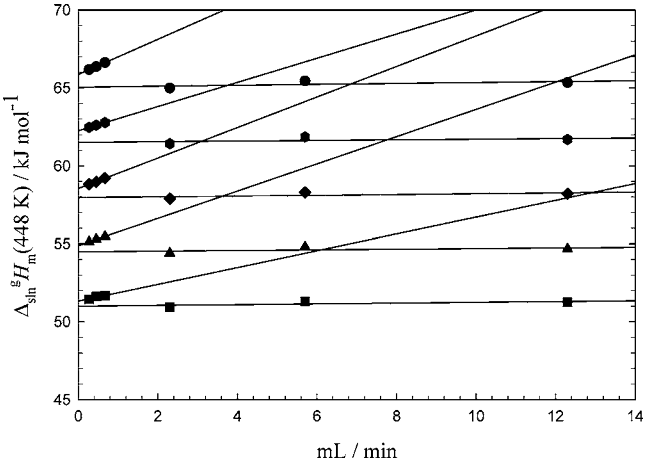

Figure 1. Effect of flow rate on the magnitude of $\Delta_{sln}{}^{g}H_m$(448 K). ■, tetradecane; ▲, pentadecane; ◆, hexadecane; ⬢, heptadecane; ●, octadecane.

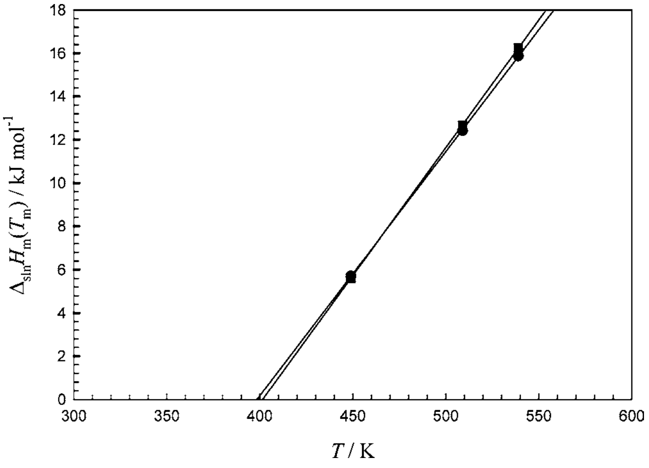

Figure 2. Effect of temperature on the magnitude of $\Delta_{sln}H_m(T/\text{K})$. ■, eicosane; ●, nonadecane.

at both T = (404 and 298.15) K, eqs 26 and 27. The enthalpies of solution of the achiral standards are no longer endothermic but rather athermal. This may be due in part to the differences in the relative proportions of the cyanopropylphenyl to dimethylsiloxane ratio present in the two columns used, but the results suggest that the achiral standards are also interacting with the *β*-cyclodextrin. The enthalpies of solution for (D)- and (L)-limonene are both slightly exothermic. The overall change in $\Delta_{sln}{}^{g}H_m(T_m)$ in going from the achiral to the chiral column is [(−6.9 ± 1.9) and (−7.7 ± 1.9)] kJ·mol^{-1}. The greater exothermicity for (D)-limonene of 0.85 kJ·mol^{-1} is sufficient to allow separation of the two enantiomers. At T = 298.15 K, the differences between the vaporization enthalpy measured ebulliometrically, (49.59 ± 0.18) kJ·mol^{-1}, and the vaporization enthalpies measured by correlation on the chiral

Table 8. Enthalpies of Transfer, Vaporization Enthalpies, and Solution of (DL)-Limonene on a 6 % Cyanopropylphenyl-/94 % Dimethylpolysiloxane Column

	−slope		$\Delta_{sln}{}^{g}H_m$(404 K)[a]	$\Delta_l{}^{g}H_m$(404 K)/kJ·mol^{-1}		$\Delta_l{}^{g}H_m$(298 K)/kJ·mol^{-1}		$\Delta_{sln}H_m$(404 K)[c]
	T	intercept	kJ·mol^{-1}	(lit)	(calcd)[b]	(lit)	(calc)[b]	kJ·mol^{-1}
octane	3889.1	10.631	32.3 ± 0.31	36.58	36.9 ± 1.1	41.56	42.1 ± 1.7	4.6 ± 1.1
nonane	4199.1	10.679	34.9 ± 0.27	40.37	40.2 ± 1.1	46.55	46.2 ± 1.8	5.3 ± 1.1
decane	4559.2	10.938	37.9 ± 0.25	44.31	44.0 ± 1.2	51.42	51.1 ± 1.9	6.1 ± 1.2
(DL)-limonene[d]	4465.7	10.354	37.1 ± 0.24		43.0 ± 1.2		49.8 ± 1.9	5.9 ± 1.2
undecane	4950.7	11.317	41.2 ± 0.24	48.3	48.2 ± 1.3	56.58	56.3 ± 2.1	7.0 ± 1.3
dodecane	5365.3	11.776	44.6 ± 0.23	52.36	52.6 ± 1.4	61.52	61.9 ± 2.2	8 ± 1.4

$$\Delta_l{}^{g}H_m(298\ \mathrm{K})/\mathrm{kJ\cdot mol^{-1}} = (1.617 \pm 0.049)\Delta_{sln}{}^{g}H_m(404\ \mathrm{K}) - (10.23 \pm 0.48) \qquad r^2 = 0.9972 \tag{24}$$

$$\Delta_l{}^{g}H_m(404\ \mathrm{K})/\mathrm{kJ\cdot mol^{-1}} = (1.28 \pm 0.03)\Delta_{sln}{}^{g}H_m(404\ \mathrm{K}) - (4.46 \pm 0.31) \qquad r^2 = 0.9982 \tag{25}$$

[a] Uncertainty calculated from the uncertainty associated with the slope of the line obtained from a ln(t_o/t_a) vs 1/*T* plot. [b] Uncertainty calculated from the uncertainty associated with the slope and intercept of eq 24 or 25. [c] $\Delta_l{}^{g}H_m$(404 K)(calc) − $\Delta_{sln}{}^{g}H_m$(404 K). [d] Literature values for (+)-limonene:[29] $\Delta_l{}^{g}H_m$(404 K), 42.69, $\Delta_l{}^{g}H_m$(298 K), (49.59 ± 0.18) kJ·mol^{-1}.

Table 9. Enthalpies of Transfer, Vaporization Enthalpies, and Solution (DL)-Limonene on a Cyclodextrin Doped 14 % Cyanopropylphenyl-/86 % Dimethylpolysiloxane Column

	−slope		$\Delta_{sln}{}^{g}H_m$(404 K)[a]	$\Delta_l{}^{g}H_m$(404 K)/kJ·mol^{-1}		$\Delta_l{}^{g}H_m$(298 K)/kJ·mol^{-1}		$\Delta_{sln}H_m$(404 K)[c]
	T	intercept	kJ·mol^{-1}	(lit)	(calcd)[b]	(lit)	(calc)[b]	kJ·mol^{-1}
octane	4447.4	11.924	36.97 ± 0.14	36.58	36.8 ± 0.7	41.56	41.9 ± 1.2	−0.2 ± 0.7
nonane	4820.4	12.013	40.08 ± 0.16	40.37	40.3 ± 0.8	46.55	46.4 ± 1.3	0.1 ± 0.8
decane	5224.1	12.315	43.43 ± 0.19	44.31	44.1 ± 0.8	51.42	51.2 ± 1.4	0.2 ± 0.8
(L)-limonene	5257.6	11.888	43.71 ± 0.20		44.4 ± 0.8		51.6 ± 1.4	−1.02 ± 0.8
(D)-limonene	5360.0	12.103	44.56 ± 0.22		45.4 ± 0.8		52.8 ± 1.4	−1.87 ± 0.8
undecane	5662.9	12.766	47.08 ± 0.21	48.30	48.2 ± 0.9	56.58	56.4 ± 1.5	0.1 ± 0.9
dodecane	6119.8	13.293	50.88 ± 0.22	52.36	52.5 ± 1.0	61.52	61.8 ± 1.6	−0.2 ± 1.0

$$\Delta_l{}^{g}H_m(404\ \mathrm{K})/\mathrm{kJ\cdot mol^{-1}} = (1.133 \pm 0.018)\Delta_{sln}{}^{g}H_m(404\ \mathrm{K}) - (5.11 \pm 0.20) \qquad r^2 = 0.9992 \tag{26}$$

$$\Delta_l{}^{g}H_m(298.15\ \mathrm{K})/\mathrm{kJ\cdot mol^{-1}} = (1.433 \pm 0.03)\Delta_{sln}{}^{g}H_m(404\ \mathrm{K}) - (11.07 \pm 0.35) \qquad r^2 = 0.9986 \tag{27}$$

[a] Uncertainty calculated from the uncertainty associated with the slope of the line obtained from a ln(t_o/t_a) vs 1/*T* plot. [b] Uncertainty calculated from the uncertainty associated with the slope and intercept of eq 26 or 27. [c] $\Delta_l{}^{g}H_m$(404 K)(calc) − $\Delta_{sln}{}^{g}H_m$(404 K).

Table 10. Enthalpies of Transfer, Vaporization Enthalpies, and Solution of (L)-Menthol on a 6 % Cyanopropylphenyl-/94 % Dimethylpolysiloxane Column

	−slope		$\Delta_{sln}{}^{g}H_m$(389 K)[a]	$\Delta_l{}^{g}H_m$(389 K)/kJ·mol^{-1}		$\Delta_l{}^{g}H_m$(298 K)/kJ·mol^{-1}		$\Delta_{sln}H_m$(389 K)[c]
	T	intercept	kJ·mol^{-1}	(lit)	(calcd)[b]	(lit)	(calc)[b]	kJ·mol^{-1}
1-hexanol	−4443.5	11.143	36.94 ± 0.25	51.48	52.1 ± 2.5	61.61	61.9 ± 1.6	15.2 ± 1.6
1-heptanol	−4822.7	11.444	40.09 ± 0.27	56.29	55.8 ± 2.7	66.81	66.3 ± 1.7	15.7 ± 1.7
1-octanol	−5240.9	11.883	43.57 ± 0.29	60.18	59.8 ± 2.9	71.00	71.2 ± 1.8	16.2 ± 1.8
(L)-menthol	−5377.7	11.577	44.71 ± 0.28		61.1 ± 3.0		72.8 ± 1.9	16.4 ± 1.9
1-decanol	−6124.3	12.942	50.92 ± 0.31	68.02	68.3 ± 3.4	81.50	81.5 ± 2.1	17.4 ± 2.1

$$\Delta_l{}^{g}H_m(389\ \mathrm{K})/\mathrm{kJ\cdot mol^{-1}} = (1.161 \pm 0.107)\Delta_{sln}{}^{g}H_m(389\ \mathrm{K}) + (9.19 \pm 0.67) \qquad r^2 = 0.9938 \tag{28}$$

$$\Delta_l{}^{g}H_m(298.15\ \mathrm{K})/\mathrm{kJ\cdot mol^{-1}} = (1.405 \pm 0.065)\Delta_{sln}{}^{g}H_m(389\ \mathrm{K}) + (9.99 \pm 0.42) \qquad r^2 = 0.9983 \tag{29}$$

[a] Uncertainty calculated from the uncertainty associated with the slope of the line. [b] Uncertainty calculated from the uncertainty associated with the slope and intercept of eq 28 or 29. [c] $\Delta_l{}^{g}H_m$(389 K)(calc) − $\Delta_{sln}{}^{g}H_m$(389 K).

column for (D)- and (L)-limonene are [(3.21 ± 1.4) and (2.01 ± 1.4)] kJ·mol^{-1}, respectively. These differences, of course, are due to the chiral interactions between the cyclodextrin and the two enantiomers and are a function of the nature of the column.

The standards used for (DL)-menthol in Table 11 were the 1-alkanols consisting of six to eleven carbon atoms except 1-nonanol. With the exception of 1-undecanol, the vaporization enthalpies used at *T* = 298.15 K are the values critically reviewed by Majer and Svoboda.[34] For 1-undecanol (used as a standard on an achiral Rtx-5 column, (Table S14, Supporting Information)), an average value of two literature values, 85.8 kJ·mol^{-1}, was used.[35] Literature vaporization enthalpies were calculated from vapor pressure generated at the temperatures of the gc experiments. For 1-hexanol, the constants of the Wagner equation, eq 6, reported by Nasirzadeh et al. (Table 2C)[25] were used, and for 1-heptanol, 1-octanol, 1-decanol, and 1-undecanol, the constants for eq 7 reported by Ambrose et al.[28] (Table 2D) were used to calculated $\Delta_l{}^{g}H_m(T_m)$. Vapor pressure values used for 1-heptanol and 1-undecanol were correlated values.[28] These equations were chosen because they were the only ones available that were applicable in the temperature range of the gc experiments.

Table 11. Enthalpies of Transfer, Vaporization Enthalpies, and Solution of (DL)-Menthol on a Rt-βDEXm Column

	−slope		$\Delta_{\text{sln}}{}^{g}H_m$(389 K)[a]	$\Delta_l{}^{g}H_m$(389 K)/kJ·mol^{-1}		$\Delta_l{}^{g}H_m$(298 K)/kJ·mol^{-1}		$\Delta_{\text{sln}}H_m$(389 K)[c]
	T	intercept	kJ·mol^{-1}	(lit)	(calcd)[b]	(lit)	(calc)[b]	kJ·mol^{-1}
n-hexanol	5774.5	14.487	48.01 ± 1.1	51.48	52.5 ± 5.2	61.61	62.3 ± 3.7	4.5 ± 5.4
n-heptanol	6089.2	14.682	50.62 ± 1.0	56.29	55.6 ± 5.5	66.81	66.1 ± 3.8	5.0 ± 5.6
n-octanol	6468.9	15.055	53.78 ± 1.0	60.18	59.4 ± 5.9	71.00	70.7 ± 4.1	5.6 ± 5.9
(D)-menthol	6839.8	15.305	56.86 ± 1.1		63.1 ± 6.2		75.2 ± 4.3	6.2 ± 6.3
(L)-menthol	6927.9	15.52	57.60 ± 1.1		64.0 ± 6.3		76.3 ± 4.4	6.4 ± 6.3
n-decanol	7383.0	16.207	61.38 ± 1.1	68.02	68.5 ± 6.7	81.50	81.8 ± 4.6	7.1 ± 6.7

$$\Delta_l{}^{g}H_m(\text{K})/\text{kJ}\cdot\text{mol}^{-1} = (1.198 \pm 0.107)\Delta_{\text{sln}}{}^{g}H_m(389\ \text{K}) - (5.028 \pm 1.70) \qquad r^2 = 0.9843 \qquad (30)$$

$$\Delta_l{}^{g}H_m(298.15)/\text{kJ}\cdot\text{mol}^{-1} = (1.453 \pm 0.074)\Delta_{\text{sln}}{}^{g}H_m(389\ \text{K}) - (7.45 \pm 0.75) \qquad r^2 = 0.9948 \qquad (31)$$

[a] Uncertainty calculated from the uncertainty associated with the slope of the line. [b] Uncertainty calculated from the uncertainty associated with the slope and intercept of eq 30 or 31. [c] $\Delta_l{}^{g}H_m$(389K)(calc) − $\Delta_{\text{sln}}{}^{g}H_m$(389K).

Table 10 summarizes the result obtained for (L)-menthol on an achiral column. A literature vaporization enthalpy at $T = 298.15$ K is not presently available. However, vapor pressures in the form of the Antoine equation for (L)-menthol are available over the temperature range $T = (372$ to $420)$ K.[29] Calculated at a mean temperature of $T = 389$ K, a vaporization enthalpy of 58.6 kJ·mol^{-1} is obtained that compares within the experimental uncertainty of the present work, (61.1 ± 3.0) kJ·mol^{-1}, calculated using correlation eq 28. The vaporization enthalpy of (DL)-menthol at $T = 298.15$ K, measured by correlation-gas chromatography on an achiral column (Rtx-5), (72.6 ± 2.9) kJ·mol^{-1},[33] is within experimental error of the value for the (L)-enantiomer, (72.8 ± 1.9) kJ·mol^{-1}. The sublimation enthalpies of both the (DL) and (L) isomers of menthol at $T = 289$ K have been measured, [(78.6 ± 4.0) and (95.8 ± 4.8)] kJ·mol^{-1}, as have their fusion enthalpies, [(10.25 and 11.88)] kJ·mol^{-1}[38] and [(12.9 ± 0.5) and (13.8 ± 0.5)] kJ·mol^{-1},[39] respectively. However, (L)-menthol is not crystalline at room temperature and probably exists in the form of a plastic crystal.[40] This suggests the presence of additional solid−solid transitions whose temperatures and magnitudes are presently not known, precluding a comparison of vaporization enthalpies. Racemic menthol may also exist in the form of a plastic crystal.

Results on the chiral column are reported in Table 11. As observed for (DL)-limonene, $\Delta_{\text{sln}}{}^{g}H_m$(389 K) values correlate quite well with $\Delta_l{}^{g}H_m$(298.15 K), eq 31. The enthalpies of solution at $T = 389$ K of all analytes are considerably less endothermic and can be considered athermal within experimental error. Unlike the results for (DL)-limonene, $\Delta_{\text{sln}}H_m$(389) values for (DL)-menthol are in line with those observed for the other 1-alkanols. This suggests that the permethylated cyclodextrin is not preferentially retaining only the chiral analytes, although it does discriminate between (D)- and (L)-menthol sufficiently to cause separation of the two enantiomers at most of the temperatures investigated. In this instance, the chiral stationary phase appears to also strongly interact with the achiral alcohols.

Discussion

The value of $\Delta_{\text{sln}}{}^{g}H_m(T_m)$ obtained by gas chromatography appears highly sensitive to temperature, the nature and history of the column, and the nature of the functional groups present on the analyte. It appears much less dependent on flow rate. The slight decrease in $\Delta_{\text{sln}}{}^{g}H_m(T_m)$ with decreasing flow rate observed may explain the differences in $\Delta_l{}^{g}H_m$(298.15 K) reported by Peacock and Fuchs when comparing values calculated by combining gc and solution studies with other methods.[18] According to eq 3, the point of intersection between $\Delta_l{}^{g}H_m$(298.15 K) determined by gas chromatography and solution studies with values obtained by other methods is 27.5 kJ·mol^{-1}. Vaporization enthalpies determined by combined gc and solution studies in excess of 27.5 kJ·mol^{-1} are predicted to slightly exceed the vaporization enthalpies obtained by other methods according to this equation. The standards used by Peacock and Fuchs to generate this relationship included various C_8 to C_{16} hydrocarbons whose vaporization enthalpies ranged from (41.5 to 80.3) kJ·mol^{-1}.[34] By extrapolating values of $\Delta_{\text{sln}}{}^{g}H_m(T_m)$ to zero flow, the slope of the line relating literature vaporization enthalpies and combined gc-solution values might be expected to increase slightly relative to the value of 0.9696 reported.

In most of the cases examined, the enthalpy of interaction of the solute with the stationary phase of the column appears both endothermic and also highly sensitive to temperature. This sensitivity to temperature and the extrapolative nature of this method offer an explanation of how it is possible to evaluate vaporization enthalpies of materials whose magnitude significantly exceeds that of the weakest bonds in the molecule. This endothermicity does not preclude attractive interactions between the analyte and the stationary phase. The endothermicity is simply a reflection of the fact that the interaction of the analyte with the column is weaker than analyte−analyte interactions. The process of condensation of the vapor on the column still remains highly exothermic. The sensitivity of $\Delta_{\text{sln}}H_m(T_m)$ to increasing temperature may be due to a decrease in the accessible surface area of both the stationary phase and analyte with increasing temperature. An increase in temperature should increase the amplitudes and populations of excited low lying vibrational frequencies which may contribute to a decrease in the accessible surface area of both the analyte and the stationary phase. This could result in a decrease in stabilizing interactions. Since the endothermicity and sensitivity to temperature appears dependent on the nature of the stationary phase, it may be possible to identify other stationary phases that would prove advantageous in extending the range of analytes, both in terms of size and functionality, that would survive passage through a gas chromatographic column upon direct injection.

Supporting Information Available:

Tables including the experimental retention times described in the text and some additional correlations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review May 13, 2009. Accepted June 18, 2009.

JE900422C