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Influence of carrier gas on the prediction of gas chromatographic retention times based on thermodynamic parameters

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A R T I C L E I N F O

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ABSTRACT

We present an investigation into the influence of carrier gas on the thermodynamics governing a capillary gas chromatographic separation. Thermodynamic parameters are estimated for a series of alkanes and alcohols on three common stationary phases using helium, hydrogen, and nitrogen carrier gases. It is shown that the substitution of carrier gases for one another results in a change in the thermodynamic parameters governing the separation. The effect of the carrier gas on the thermodynamic parameters is large enough to compromise the accuracy of the retention time calculations based on thermodynamic parameters collected in a carrier gas other than the one actually in use in a specific gas chromatographic system. A possible kinetic explanation for these observations is also investigated.

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1. Introduction

There are numerous instances where the prediction of gas chromatographic retention times for compounds would be useful. Most obviously would be for accelerating the optimization of instrumental conditions for a given analysis, or selecting the stationary phase for a separation. Without a mathematical model, these optimizations can be time consuming and a model with good predictive abilities for a range of compounds on a range of stationary phases would greatly increase the ease of optimization. Modeling of gas chromatographic retention parameters (retention index, relative retention, or retention time) can also be useful in conjunction with a mass spectrometer to identify unknown components in a sample. Such information is especially useful in isomer identification where mass spectra alone are often unable to distinguish similar species.

There are a variety of predictive models that have found use in the field of gas chromatography, where they are used for estimating retention time, relative retention or Kovats retention index. Many of these predictive models fall into the category of quantitative structure-retention relationships (QSRRs) which, through the use of multiple linear regression or artificial neural networks correlate molecular descriptors to a specific retention parameter such as retention index or retention factor. These models have been used previously to determine retention parameters for a host of analytes including alkanes/alkenes [1], alkylbenzenes [2], alcohols [3], and esters [4]. Analytes including polyaromatic hydrocarbons [5] as well as various compounds of environmental concern such as PCBs [6,7] and pesticides [8,9] have also been related to retention parameters using QSRR models.

A second form of predictive model relies on boiling point-retention time correlations. The abundance of boiling point data in the literature and the correlation between boiling point and elution order for many compounds on non-polar stationary phases explain the popularity of this approach. These models have found application in studies of halogenated hydrocarbons [10], alkylbenzenes [11,12], methylbenzenes [13], and substituted phenols [14]. A final approach to retention modeling is the use of additive rules. These models break a molecule up into a series of substituents or smaller molecules for which the influences on retention are known. Through a mathematical combination of the substituents, the retention parameter of interest can be predicted. This approach has been used recently with both retention index predictions [15] and predictions of retention time based on thermodynamic parameters [16].

Recent interest in predictive modeling has also focused on using thermodynamics to predict the retention times of various analyte classes on several types of stationary phases [17–20]. One advantage of thermodynamic models is that if the thermodynamics can be modeled precisely, then the retention time of an analyte can be predicted directly, independent of operating conditions, unlike properties such as the retention index, which can vary with temperature and temperature programming rate. Thermodynamic parameters are easily obtained from isothermal experiments on any gas chromatograph and can be modeled for many different classes of compounds. Previous studies have focused on the basic calculations of these thermodynamic models and validation of their predictive abilities [16–18,21]. The results of these studies have shown that the use of thermodynamics in the prediction

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^{0021-9673/\$ -} see front matter © 2010 Elsevier B.V. All rights reserved. doi:10.1016/j.chroma.2010.09.068

Table 1

Column geometries and corresponding phase ratios used for the kinetic influence study. All five columns were 30 m in length and were coated with SLB5ms (5% phenyl substituted polydimethylsiloxane) stationary phase.

Internal diameter (mm)	Film thickness (µm)	Phase ratio
0.10	0.10	2.5×10^2
0.20	0.20	$2.5 imes 10^2$
0.25	0.25	$2.5 imes 10^2$
0.32	0.32	$2.5 imes 10^2$
0.53	0.50	$2.7 imes 10^2$

of retention time can be accurate for several different classes of analytes on a range of stationary phase chemistries. The various mathematical models used to calculate the thermodynamic parameters used in these models have also been extensively investigated [16,17,19,21–23]. In this work the three thermodynamic parameters of enthalpy (ΔH), entropy (ΔS), and adiabatic molar heat capacity (ΔC_p), were used to investigate the effect of carrier gas on thermodynamic predictions.

In considering the factors that influence a GC separation, conventional wisdom dictates that changing the carrier gas will have a rather large effect on the kinetics of a separation but an insignificant effect on the separation's thermodynamics; i.e. knowledge of the thermodynamic parameters for a given compound on a given stationary phase will permit accurate predictions for the molecule, irrespective of the carrier gas used (assuming one accounts for the changes in kinetics). In this research, we explore the assumption that thermodynamic parameters that are obtained for a variety of compounds on a series of stationary phases when using helium, hydrogen, and nitrogen carrier gases. We also investigate the effect of column diameter on the determination of ΔH , ΔS , and ΔC_p to probe the possibility of kinetic effects that could impact the determination of the thermodynamics in different carrier gases. This is a reasonable question as GC is a dynamic experiment where thermodynamic parameters are being inferred from a system that is not permitted to reach equilibrium.

2. Experimental

Experiments were carried out on a Varian 3800 GC (Varian Inc., Mississauga, ON) equipped with a flame ionization detector and a split/splitless injector using a split ratio of 50:1. The injector and detector were both maintained at 230 °C. The phases of the columns studied were SLB5ms, SPB50 (polydimethysiloxane with 5%, and 50% phenyl substitution, respectively), and Supelcowax (polyethylene glycol) purchased from Supelco (Oakville, ON).

For carrier gas investigations, all columns had a nominal geometry of (30 m × 0.25 mm; 0.25 µm film thickness). For investigation of the influence of column geometry, experiments were carried out on five SLB5ms columns with the dimensions shown in Table 1. All separations were conducted isothermally and the pressure was adjusted such that the average linear velocity of the carrier gas was 30, 40, or $15 \,\mathrm{cm\,s^{-1}}$ for He, H₂, or N₂ carrier gases, respectively.

Two sample mixtures of compounds were used to test different carrier gases. The first was a solution containing 2-methylhexane, 2,4-dimethylhexane, 2,3-dimethylheptane, and 2,6-dimethyloctane (Sigma–Aldrich, Oakville, ON) at concentrations of 250–1000 ppm in pentane. The second mixture comprised 3-hexanol, 3-methyl-1-pentanol, 4-methyl-1-hexanol, 4-nonanol,

Table 2

Thermodynamic parameters collected for several alcohols and alkanes using three stationary phases and three carrier gases.

Compound	Phase	Carrier gas	ΔH (kJ mol ⁻¹)	ΔS (J K ⁻¹ mol ⁻¹)	$\Delta C_p (\mathrm{J}\mathrm{K}^{-1}\mathrm{mol}^{-1})$
2-Methylhexane	SPB50	Не	-26.472	-45.420	30.319
-		H ₂	-26.472	-45.420	35.269
		N ₂	-25.627	-43.016	48.061
	SLB5ms	He	-28.838	-48.072	60.547
		H ₂	-28.643	-47.346	58.029
		N ₂	-28.595	-47.233	52.761
	Supelcowax	He	-19.588	-32.130	92.391
		H ₂	-18.489	-28.826	101.329
		N ₂	-20.832	-35.554	25.115
2,6-Dimethyloctane	SPB50	He	-36.341	-57.669	55.746
-		H ₂	-36.098	-57.057	62.068
		N ₂	-36.033	-56.921	61.772
	SLB5ms	He	-39.996	-62.944	72.066
		H ₂	-39.980	-62.763	69.359
		N ₂	-39.895	-62.571	71.292
	Supelcowax	He	-30.646	-49.103	50.935
	-	H ₂	-30.310	-48.153	46.771
		N ₂	-30.113	-47.698	53.889
4-Nonanol	SPB50	He	-46.228	-71.356	85.395
		H ₂	-45.631	-69.852	77.301
		N ₂	-45.679	-69.992	83.344
	SLB5ms	He	-47.137	-73.326	90.583
		H ₂	-46.858	-72.670	83.934
		N ₂	-46.824	-72.572	85.695
	Supelcowax	He	-51.392	-78.102	93.406
		H ₂	-51.414	-78.193	96.592
		N ₂	-51.354	-78.093	98.767
3-Hexanol	SPB50	He	-34.939	-56.316	71.925
		H ₂	-33.944	-53.659	65.020
		N ₂	-34.040	-53.894	74.377
	SLB5ms	He	-34.818	-56.657	77.467
		H ₂	-34.469	-55.772	75.780
		N ₂	-34.060	-54.629	66.810
	Supelcowax	He	-41.216	-64.485	81.202
		H ₂	-41.177	-64.360	86.006
		N ₂	-41.014	-63.953	86.780

Table 3

Regression statistics for predicted vs. actual retention time using He thermodynamic parameters for the estimation of retention time of analytes in three different carrier gases. df = degrees of freedom; N/A = not applicable.

Analyte	Phase	Carrier gas used	Slope <i>m</i> (error)	Intercept <i>b</i> (error)	df	<i>t</i> -Statistic 99.9% (critical value 3.883 df = 19)
2-Methylhexane	SPB50	Не	0.999 (0.002)	0.003 (0.004)	49	N/A
-		H ₂	$1.005(0.004)^{*}$	-0.008 (0.007)	52	14.4
		N ₂	1.022 (0.001)*	-0.096 (0.002)	52	147.4
	SLB5ms	He	1.009 (0.001)	-0.019(0.002)	67	N/A
		H ₂	$1.001 (0.001)^{*}$	-0.002 (0.001)	67	31.6
		N ₂	$0.995(0.001)^{*}$	0.012 (0.004)	63	61.3
	Wax	He	0.995 (0.017)	0.01 (0.04)	19	N/A
		H ₂	0.994 (0.025)	0.01 (0.04)	19	1.0
		N ₂	$1.064(0.007)^{*}$	-0.25 (0.03)	22	142.3
2,6-Dimethyloctane	SPB50	He	1.001 (0.001)	-0.005(0.004)	52	N/A
		H ₂	$1.013(0.001)^{*}$	-0.023(0.002)	52	25.9
		N ₂	$1.023~(0.000)^{*}$	-0.113 (0.005)	52	49.0
	SLB5ms	He	1.007 (0.001)	-0.026(0.005)	67	N/A
		H ₂	$0.989(0.001)^{*}$	0.007 (0.003)	67	29.2
		N ₂	$0.993(0.000)^{*}$	0.015 (0.003)	63	31.7
	Wax	He	1.000 (0.001)	0.000 (0.003)	31	N/A
		H ₂	$1.027 \left(0.002 ight)^{*}$	-0.049(0.005)	31	60.5
		N ₂	$1.039(0.001)^{*}$	-0.181 (0.009)	31	80.1
3-Hexanol	SPB50	He	1.001 (0.001)	-0.002(0.003)	49	N/A
		H ₂	$1.017 \left(0.001 ight)^{*}$	-0.030(0.002)	49	80.7
		N ₂	$1.017 \left(0.001 ight)^{*}$	-0.092(0.006)	49	74.6
	SLB5ms	He	1.007 (0.003)	-0.017 (0.006)	49	N/A
		H ₂	$1.012(0.001)^{*}$	-0.020(0.002)	49	12.5
		N ₂	$1.010(0.001)^{*}$	-0.053 (0.006)	43	10.1
	Wax	He	1.000 (0.001)	0.000 (0.002)	49	N/A
		H ₂	1.000 (0.001)	-0.003 (0.001)	49	0.4
		N ₂	$1.005~(0.000)^{*}$	0.033 (0.001)	49	38.9
4-Nonanol	SPB50	He	1.000 (0.001)	0.000 (0.004)	49	N/A
		H ₂	$1.018(0.001)^{*}$	-0.037(0.002)	49	37.6
		N ₂	$1.020(0.001)^{*}$	-0.126 (0.006)	49	42.8
	SLB5ms	He	1.000 (0.000)	0.000 (0.002)	49	N/A
		H ₂	$1.014(0.000)^{*}$	-0.024(0.002)	49	57.8
		N ₂	$1.013(0.000)^{*}$	-0.069(0.004)	43	57.5
	Wax	He	1.000 (0.000)	0.000 (0.002)	49	N/A
		H ₂	$1.005 \left(0.000 ight)^{*}$	-0.117 (0.002)	49	16.9
		N ₂	$1.013~(0.000)^{*}$	-0.076 (0.002)	49	65.0

* Statistically significant differences between He regression and the carrier gas used at 99.9% confidence.

2-nonanol, 2-methyl-5-nonanol, and 5-decanol (Aldrich) at concentrations of 250–1000 ppm in methylene chloride.

The samples used for investigating the effect of column diameter were a mixture of n-alkanes and a mixture of alcohols. The alkane mixture comprised undecane (Fisher, Ottawa, ON), dodecane (Eastman, Rochester, NY), tridecane (Aldrich), and tetradecane (Eastman) in pentane. The alcohol mixture consisted of a mixture of 1-undecanol (Aldrich), 1-dodecanol (Eastman), 1-tridecanol, and 1-tetradecanol (Aldrich) in 2-butoxyethanol.

For all experiments, injections were carried out in triplicate using 1 μL of standard solution with a co-injection of ${\sim}5\,\mu L$ of methane as a dead time marker.

3. Results and discussion

3.1. Effect of carrier gas

By using data from a series of isothermal runs and a threeparameter thermodynamic model [21], the values for $\Delta H(T_0)$, $\Delta S(T_0)$, and ΔC_p can be determined for each analyte. These values can then be used to predict the partition coefficient, and hence retention time, for the given analyte on a specific stationary phase, at any temperature, with a high degree of precision and accuracy [16]. In order to investigate the effect of carrier gas on the thermodynamic parameters that govern GC retention, a series of experiments similar to those that we have used previously [16] were performed. Here, each solution was tested isothermally on each of the three column phases, across a range of temperatures and using each of the three carrier gases under study (H₂, He, N₂). In this work, the reference temperature (T_0) was arbitrarily chosen to be 90 °C. For the ease of readability, $\Delta H(T_0)$ and $\Delta S(T_0)$ will be referred to as ΔH and ΔS for the remainder of this work; the reference temperature of T_0 being implied.

Table 2 presents the thermodynamic parameters that were determined for several alkanes and alcohols on all stationary phases and carrier gases. These data sets are typical of what was observed for most compounds. As can be seen in Table 2, the values for ΔH and ΔS are reasonably consistent for a given stationary phase, regardless of the carrier gas that is used. This is consistent with what would be expected. The carrier gas would make little difference to the enthalpy or entropy of a gas phase molecule, and have no influence over these parameters when the molecule was sorbed into the stationary phase. Consequently, the magnitudes of ΔH and ΔS are dictated almost solely by the chemistries of the analyte and the stationary phase.

This is contrasted by the behavior of ΔC_p , which shows relatively large fluctuations as the carrier gas is changed. One possible explanation for this is that the change in isobaric molar heat capacity of the molecule when it moves from one phase to the other will depend on the amount of energy required to change its vibrational and rotational states in both the stationary and mobile phases. This will in turn depend at least in part on how much resistance to vibration and rotation the molecule experiences in both phases, and for the gas phase this will depend on the nature of the carrier gas. Consequently, ΔC_p will depend on the nature of both the stationary and mobile phases. What is surprising is the magnitude of the influence

Table 4

Root mean square error of prediction for predicted vs. actual retention time when using He thermodynamics to predict isothermal retention times of analytes in the three carrier gases under study.

2-Methylhexane SPB50 He 0.183 40-120 H2 0.295 N2 0.538 5LB5ms He 0.324 50-150 H2 0.100 N2 0.718 Wax He 0.283 40-70	
H2 0.295 N2 0.538 SLB5ms He 0.324 50-150 H2 0.100 N2 0.718 Wax He 0.283 40-70	
N2 0.538 SLB5ms He 0.324 50-150 H2 0.100 N2 0.718 Wax He 0.283 40-70	
SLB5ms He 0.324 50-150 H2 0.100 N2 0.718 Wax He 0.283 40-70	
H ₂ 0.100 N ₂ 0.718 Wax He 0.283 40-70	
N2 0.718 Wax He 0.283 40-70	
Wax He 0.283 40-70	
н ₂ 0.238	
N ₂ 0.422	
2,6-Dimethyloctane SPB50 He 0.764 40–125	
H ₂ 1.794	
N ₂ 8.484	
SLB5ms He 2.696 40–150	
H ₂ 3.723	
N ₂ 4.540	
Wax He 0.224 40-90	
H ₂ 1.044	
N ₂ 4.752	
3-Hexanol SPB50 He 0.130 90–170	
H ₂ 0.230	
N ₂ 0.838	
SLB5ms He 0.387 80–160	
H ₂ 0.221	
N ₂ 0.379	
Wax He 0.134 100-180	
H ₂ 0.215	
N ₂ 0.616	
4-Nonanol SPB50 He 0.601 90-170	
H ₂ 1.518	
N ₂ 4.724	
SLB5ms He 0.355 90–160	
H ₂ 2.443	
N ₂ 3.947	
Wax He 0.477 100–180	
H ₂ 0.730	
N ₂ 4.838	

that the carrier gas has on this term for some molecules. A second possible explanation for some of the behavior of ΔC_p is that it is an artifact of the regression process, as ΔC_p is a minor term and the regression is dominated by ΔH and ΔS , an inordinate amount of the error may be forced into ΔC_p .

The accuracy of retention time predictions that can be made if one uses thermodynamic parameters derived in one carrier gas to make predictions of retention in a different carrier gas were evaluated by using helium as a reference gas. The thermodynamic parameters for a molecule in helium were used to predict the retention times for molecules in both nitrogen and hydrogen carrier gases across a range of temperatures. The predictions were made based on the ΔH , ΔS , and ΔC_p terms obtained for helium which were then used to calculate the parameters a_0 , a_1 , and a_2 in Eqs. (1)–(3). Then the partition coefficient at a given temperature was predicted using Eq. (4) [17]:

$$a_0 = \frac{\Delta S(T_o) - \Delta C_p \cdot \ln T_o - \Delta C_p}{R}$$
(1)

$$a_1 = -\frac{\Delta H(T_o) - \Delta C_p \cdot T_o}{R} \tag{2}$$

$$a_2 = \frac{\Delta C_p}{R} \tag{3}$$

$$\ln K = a_0 + a_1 \cdot \frac{1}{T} + a_2 \cdot \ln T \tag{4}$$

Once the partition coefficient was predicted for a given temperature, the retention factor and then the retention time were predicted based on this value, the dead time, and the nominal phase ratio for the column (Eqs. (5)-(7)):

$$\beta = \frac{r_c}{2d_f} \tag{5}$$

$$k = \frac{K}{\beta} \tag{6}$$

$$k = \frac{t_r - t_m}{t_m} \tag{7}$$

Table 3 presents the results of these comparisons for a sample of the test molecules. The results are presented as slopes and intercepts of the lines of measured vs. predicted retention times for each gas. For helium carrier gas, the slopes and intercepts of all lines were expectedly 1.000 and 0.000, indicating that the predicted and measured retention times were near identical when the thermodynamic parameters were matched to the gas being used to perform the separations. Using the helium thermodynamic values to predict the retention times in nitrogen or hydrogen, a similar comparison can be made and any deviation in the slope or intercept of the line will be indicative of a difference between the predicted and measured retention times. When the thermodynamic parameters were not matched to the gas being used to perform the separations it was found that the slopes of these lines differed from 1.000 and 0.000. The errors associated with the slope and intercept are indicated in Table 3 as one standard deviation estimated by the linear regression. The regressions for hydrogen vs. helium and nitrogen vs. helium were compared to the lines for the helium vs. helium regression using a *t*-test for comparing regression lines [24]. Cases where the lines were found to deviate with statistical significance, i.e. where the calculated *t*-value was greater than the critical *t*-

Table 5

Thermodynamic parameters collected in helium in relation to column diameter.

1-Undecanol0.10-9.771-9.8249.900.20-58.33-87.61105.620.25-58.43-87.79108.930.32-58.45-87.57110.120.33-86.47-91.93102.320.44-61.83-91.93102.320.25-62.56-93.52114.090.26-62.59-93.52113.030.27-62.59-91.88105.271.17 idecanol0.03-66.59-91.880.32-66.65-91.88105.270.33-66.64-99.29116.310.30-66.65-99.16118.020.32-66.63-99.16118.020.32-66.63-99.16118.020.32-66.64-99.29116.310.33-66.47-97.0311.050.34-66.47-97.0311.050.35-70.75-104.8512.150.36-70.76-105.0312.150.36-70.75-103.6011.650.35-70.37-103.60116.890.35-46.72-71.1383.360.36-69.41-70.9883.350.37-60.46-70.9883.350.38-60.47-70.7587.220.39-46.65-69.4166.330.46.65-69.41-68.330.46.65-69.41-68.330.46.65-69.41-68.330.46.65-69.41-68.34	Analyte	Column i.d. (mm)	ΔH (kJ mol ⁻¹)	ΔS (J K ⁻¹ mol ⁻¹)	ΔC_p (J K ⁻¹ mol ⁻¹)
1-Dodecanol0.20-88.30-87.61105.620.32-88.43-87.73100.320.32-88.45-87.73100.230.10-61.83-91.93102.320.20-62.36-93.23108.170.25-62.56-93.52114.090.32-62.39-92.85113.030.42-62.56-93.16105.71-Tridecanol0.10-65.93-97.620.53-66.64-99.16113.500.54-66.65-99.16113.500.53-66.74-97.08106.981-Tertadecanol0.53-66.47-97.080.53-66.47-97.08106.981-Tertadecanol0.53-70.76-105.031-Tertadecanol0.53-70.76-105.030.53-70.76-104.85122.570.54-46.72-71.1333.360.55-46.67-70.9876.620.53-70.37-104.86122.570.54-46.72-71.1333.360.55-46.67-70.9878.660.54-70.9876.5677.620.55-70.55-74.6476.920.54-50.91-75.5837.460.55-50.92-75.4833.990.54-50.92-75.4833.990.55-50.92-75.8839.300.54-50.92-75.8839.300.55-50.92-75.8839.	1-Undecanol	0.10	-57.71	-86.24	97.90
1-Dodecanol025-88.43-87.79108.931-Dodecanol0.53-88.07-87.57101.011-Dodecanol0.10-61.33-91.93109.731-Dodecanol0.20-62.39-93.23109.731-Dodecanol0.25-62.56-93.52113.031-Tridecanol0.53-62.56-91.88105.271-Tridecanol0.63-66.64-99.29116.311-Tridecanol0.63-66.64-99.29106.721-Tetradecanol0.10-70.00-103.25111.051-Tetradecanol0.10-70.00-103.25111.051-Tetradecanol0.10-70.07-105.03122.571-Tetradecanol0.10-70.07-105.03122.571-Tetradecanol0.10-70.75-104.85122.571-Tetradecanol0.10-70.75-104.85122.571-Tetradecanol0.10-70.03121.05105.271-Tetradecanol0.10-70.75-104.85122.571-Tetradecanol0.10-70.75-104.85122.571-Tetradecanol0.10-70.75-70.76105.291-Tetradecanol0.10-70.75-70.76105.291-Tetradecanol0.10-70.9537.4633.561-Tetradecanol0.10-50.90-70.9537.461-Tetradecanol0.10-50.90-70.9537.461-Tetradecanol0.10-50.91-76.9537		0.20	-58.30	-87.61	105.62
1-Dodecanol0.32-88.45-87.5711.10.121-Dodecanol0.10-61.83-91.93102.320.20-62.39-93.23109.730.25-62.36-93.52114.090.26-62.36-91.88105.271-Tridecanol0.10-65.93-97.62106.720.25-66.65-99.16118.020.26-66.64-99.29116.310.27-66.65-99.16118.020.28-66.67-97.08106.921-Tetradecanol0.10-70.00-103.25111.050.20-70.75-104.85122.570.23-70.75-104.85122.570.24-70.73-103.60116.890.25-70.75-104.85122.570.26-70.75-104.85122.570.27-70.38-102.27108.920.28-70.38-102.77108.920.29-46.70-70.9833.350.20-46.72-71.1383.360.21-46.65-69.4165.330.22-50.90-76.5587.460.25-50.90-76.5883.590.25-50.92-76.7687.720.25-50.92-76.7687.720.25-50.92-76.78839.910.26-55.12-82.9293.490.27-55.12-82.9293.490.28-55.12-82.9293.490.2		0.25	-58.43	-87.79	108.93
1-Dodecanol 0.33 -58.07 -85.17 91.47 1-Dodecanol 0.00 -61.83 -91.93 102.32 0.20 -62.39 -93.32 109.73 0.25 -62.56 -93.52 114.09 0.32 -62.39 -92.85 113.03 0.53 -62.56 -91.88 105.27 0.63 -66.64 -99.92 116.31 0.25 -66.65 -99.16 118.02 0.26 -66.66 -99.16 118.02 0.25 -66.67 -99.16 118.02 0.26 -70.076 -105.03 11.05 0.27 -70.076 -105.03 11.05 0.26 -70.775 -104.85 122.57 0.32 -70.37 -103.60 116.89 0.26 -70.737 -103.60 168.92 0.10 -46.61 -70.98 83.35 0.25 -46.65 -99.41 86.33 0.26 -50.67		0.32	-58.45	-87.57	110.12
1-Dedecanol0.10-61.83-91.93102.320.26-62.39-93.23109.730.25-62.56-93.52114.090.32-62.39-92.85113.031-Tridecanol0.10-65.93-97.62106.720.26-66.65-99.16118.020.27-66.65-99.16118.020.28-66.65-99.16118.020.29-66.64-99.2916.310.20-66.64-99.16118.020.32-66.30-98.01113.501-Tetradecanol0.10-70.76-103.03121.650.20-70.75-104.85122.570.21-70.75-104.85122.570.22-70.38-70.3870.820.33-70.38-70.22108.920.46.72-71.1383.360.25-46.65-99.4183.350.26-50.90-76.9587.460.27-70.8875.5646.530.28-50.90-76.5587.460.29-50.56-76.5587.460.20-50.51-88.5795.6417-59.15-75.7883.5917-63.24-75.1883.5917-63.24-88.5795.6417-59.51-88.5795.6417-59.51-88.5795.6417-59.51-88.5795.6416-59.51-88.5795.64		0.53	-58.07	-85.17	91.47
0.20-62.39-93.23109.730.25-62.56-93.52114.090.32-62.39-92.85113.031-Tridecanol0.53-62.56-91.88105.270.20-66.64-99.29116.310.21-66.65-99.16118.020.22-66.66-99.16118.020.23-66.30-98.01113.500.24-66.37-97.08106.720.25-66.67-99.16118.020.26-70.76-103.25111.050.27-70.76-104.85122.570.28-70.77-104.85122.570.29-70.76-105.03121.050.20-70.76-104.85128.920.21-70.73-104.85128.920.22-70.75-104.85128.920.23-70.37-103.60116.890.24-70.73-103.60116.890.25-70.75-70.4883.350.25-46.67-70.9883.350.25-46.67-70.9883.350.25-50.54-75.8883.590.25-50.54-75.8883.590.26-50.55-82.6393.0117idecane0.32-55.05-82.6393.0117idecane0.32-55.05-82.6393.0117idecane0.32-55.05-82.6393.0117idecane0.32-55.05-82.6393.01 <tr< td=""><td>1-Dodecanol</td><td>0.10</td><td>-61.83</td><td>-91.93</td><td>102.32</td></tr<>	1-Dodecanol	0.10	-61.83	-91.93	102.32
0.25-62.56-93.52114.090.32-62.56-91.88105.271-Tridecanol0.10-65.93-97.62106.720.20-66.65-99.16118.020.22-66.65-99.16118.020.32-66.67-99.16118.020.32-66.47-97.08106.981-Tetradecanol0.10-70.00-105.03121.050.53-66.47-90.63121.0511.050.54-70.75-104.85122.050.53-70.75-104.85122.050.32-70.76-105.03121.050.32-70.37-103.60116.890.32-70.38-102.27108.920.46.61-70.9883.360.53-46.65-69.4186.330.53-46.65-69.4186.330.54-59.15-88.5795.640.55-50.52-75.7687.720.54-50.52-75.7893.9817idecane0.10-54.96-82.6689.480.53-50.52-75.7893.9817idecane0.10-54.95-88.5793.9317idecane0.10-59.15-88.5793.490.53-50.54-81.54101.3717idecane0.10-59.15-88.5795.640.53-50.54-88.5795.640.53-50.54-88.5795.640.54-55.15-88.57		0.20	-62.39	-93.23	109.73
1-Tridecanol0.32-62.39-92.8511.3031-Tridecanol0.10-65.93-97.62106.720.20-66.64-99.29116.310.25-66.65-99.16118.020.26-66.64-99.29116.310.32-66.30-98.01113.500.33-66.47-97.08106.981-Tetradecanol0.10-70.00-103.25111.050.25-70.75-104.8522.570.26-70.75-104.8522.570.32-70.38-102.27108.920.46-70.9833.66-98.100.53-70.37-103.60118.890.10-46.61-70.9833.660.25-46.70-70.9883.350.26-46.70-70.9883.350.270.33-50.59-76.7687.720.33-50.59-76.7585.640.26-50.90-76.7585.640.27-51.51-88.5795.640.28-50.52-75.4893.9817idecane0.10-59.15-88.5795.640.25-50.51-82.6393.0117idecane0.13-59.15-82.6393.0117idecane0.10-59.15-82.6393.0117idecane0.10-59.15-82.6393.0117idecane0.10-59.15-82.6393.0117idecane0.10-59.15-82.6393.0		0.25	-62.56	-93.52	114.09
1-Tridecanol0.53-62.56-91.88105.271-Tridecanol0.10-65.93-97.620.16.720.20-66.64-99.29116.310.25-66.65-99.16118.020.32-66.30-98.0111.500.32-66.47-97.08106.981-Tetradecanol0.10-70.00-103.25111.050.20-70.76-105.03121.050.20-70.76-103.60116.890.21-70.37-104.85122.570.32-70.37-103.60116.890.32-70.37-103.60116.890.46-70.9838.36-102.270.46-70.9838.36-102.270.53-46.65-69.4186.330.54-50.50-76.5587.460.53-50.50-76.5587.460.54-50.50-75.5885.590.53-50.51-88.5795.640.54-55.12-88.5795.640.55-55.05-82.6693.9117idecane0.10-55.12-88.5795.640.51-55.15-88.5795.640.52-55.05-82.6693.910.53-55.15-88.5795.640.54-55.15-88.5795.640.55-55.15-88.5795.640.52-55.15-88.5795.640.53-55.15-88.5795.640.54		0.32	-62.39	-92.85	113.03
1-Tridecanol 0.10 -65.93 -97.62 106.72 0.20 -66.64 -99.29 116.31 0.25 -66.65 -99.16 118.02 0.32 -66.63 -99.16 118.02 0.53 -66.47 -97.08 106.98 1-Tetradecanol 0.10 -70.00 -103.25 111.05 0.20 -70.75 -104.85 122.57 0.32 -70.37 -103.60 116.89 0.53 -70.38 -102.27 108.92 0.40 -46.61 -70.98 78.66 0.20 -46.72 -71.13 83.36 0.20 -46.67 -70.94 76.92 0.32 -46.66 -69.41 86.33 0.20 -50.515 -88.57 56.4 0.20 -50.87 -76.75 87.46 0.21 -50.64 -75.88 83.59 0.32 -50.44 -75.88 93.93 1ridecane 0.10		0.53	-62.56	-91.88	105.27
020 -66.64 -92.92 116.31 0.25 -66.65 -99.16 118.02 0.32 -66.30 -98.01 113.50 0.53 -66.47 -97.08 106.98 1-Tetradecanol 0.10 -70.00 -103.25 111.05 0.20 -70.76 -105.03 121.05 0.25 -70.75 -104.85 122.57 0.32 -70.37 -103.60 116.89 0.45 -70.37 -103.60 108.92 0.46.41 -70.98 78.66 0.20 -46.72 -71.13 83.36 0.22 -46.61 -70.98 83.35 0.23 -46.62 -69.41 86.33 0.24 -50.50 -75.76 77.72 0.25 -50.87 -76.76 87.72 0.26 -50.50 -75.88 33.59 0.25 -50.87 -75.76 87.72 0.26 -55.12 -82.63 93.01	1-Tridecanol	0.10	-65.93	-97.62	106.72
0.25 -66.65 -99.16 118.02 1-Tetradecanol 0.32 -66.30 -98.01 113.50 0.53 -66.47 -97.08 106.98 1-Tetradecanol 0.10 -70.076 -105.03 121.05 0.20 -70.75 -104.85 122.57 0.32 -70.37 -103.60 116.89 0.53 -70.38 -102.27 108.92 0.10 -46.61 -70.98 78.66 0.20 -46.70 -71.13 83.36 0.25 -46.62 -70.04 76.92 0.25 -46.65 -60.41 86.33 0.25 -46.65 -60.41 86.33 0.26 -50.87 -76.95 87.46 0.20 -50.87 -76.95 87.46 0.20 -50.87 -76.75 87.72 0.32 -50.64 -75.88 83.59 0.45 -50.92 -75.48 93.91 104 -59.15 <t< td=""><td></td><td>0.20</td><td>-66.64</td><td>-99.29</td><td>116.31</td></t<>		0.20	-66.64	-99.29	116.31
0.32-66.30-98.01113.501-Tetradecanol0.53-66.47-97.08106.981.0-70.00-103.25111.050.20-70.76-105.03121.050.25-70.75-104.85122.670.32-70.37-103.60116.890.32-70.38-102.27108.920.46.71-70.9883.360.20-46.72-71.1383.360.32-46.66-60.4166.330.32-46.65-60.4186.330.53-46.65-60.4186.330.53-50.87-76.9587.460.53-50.87-76.9587.460.20-50.87-76.9587.460.21-50.87-76.9587.460.22-50.64-75.8883.5917idecane0.10-54.96-82.6689.480.53-50.51-82.9293.4917idecane0.10-59.15-82.6689.480.22-50.51-82.6689.48103-55.12-82.9293.49104-59.15-88.5795.641053-55.18-81.54101.371053-55.18-81.54101.371053-55.18-81.54101.371053-55.18-81.54101.371053-55.18-81.54101.371053-55.18-81.54101.371053-55.18-81.54101.37		0.25	-66.65	-99.16	118.02
1-Tetradecanol 0.53 -66.47 -97.08 106.98 1-Tetradecanol 0.10 -70.00 -103.25 111.05 0.20 -70.76 -106.50.3 121.05 0.25 -70.75 -104.85 122.57 0.32 -70.37 -103.60 116.89 0.53 -70.38 -102.27 108.92 Undecane 0.10 -46.61 -70.98 78.66 0.20 -46.72 -71.13 83.36 0.25 -46.70 -70.98 83.35 0.25 -46.65 -69.41 86.33 0.20 -59.15 -88.57 95.64 0.20 -50.90 -76.95 87.46 0.20 -50.87 -75.76 87.72 0.32 -50.64 -75.88 83.59 0.25 -50.50 -82.66 89.48 0.20 -55.12 -82.92 93.49 0.25 -55.50 -82.66 89.48 0.20		0.32	-66.30	-98.01	113.50
1-Tetradecanol 0.10 -70.00 -103.25 111.05 0.20 -70.76 -105.03 121.05 0.25 -70.75 -104.85 122.57 0.32 -70.38 -102.27 108.92 0.53 -70.78 -70.98 78.66 0.20 -46.61 -70.98 78.66 0.20 -46.72 -71.13 83.36 0.25 -46.65 -69.41 86.33 0.25 -46.65 -69.41 86.33 0.26 -50.90 -75.85 87.46 0.20 -50.90 -75.45 87.46 0.25 -50.87 -76.76 87.72 0.26 -50.92 -75.48 93.98 0.25 -50.64 -75.88 83.59 0.20 -55.12 -82.62 93.01 0.20 -55.12 -82.63 93.01 0.25 -55.51 -82.63 93.01 0.26 -55.18 -81.54 101.37 <td></td> <td>0.53</td> <td>-66.47</td> <td>-97.08</td> <td>106.98</td>		0.53	-66.47	-97.08	106.98
0.20 -70.76 -105.03 121.05 0.25 -70.37 -104.85 122.57 0.53 -70.38 -102.27 108.92 Undecane 0.10 -46.61 -70.98 78.66 0.20 -46.72 -71.13 83.36 0.20 -46.62 -70.98 83.35 0.20 -46.65 -69.41 86.33 0.21 -50.90 -76.55 87.46 0.22 -50.64 -75.88 83.59 0.22 -50.64 -75.88 83.59 0.22 -50.64 -75.88 83.59 0.23 -50.64 -75.88 83.59 0.25 -50.67 -76.76 87.72 0.25 -50.62 -75.48 93.98 17ridecane 0.10 -54.96 -82.66 89.48 0.20 -55.12 -82.63 93.01 101 -54.96 -82.66 89.48 102 -55.18 -81.54	1-Tetradecanol	0.10	-70.00	-103.25	111.05
0.25 -70.75 -104.85 122.57 0.32 -70.37 -103.60 116.89 0.53 -70.38 -102.27 108.92 0.10 -46.61 -70.98 78.66 0.20 -46.72 -71.13 83.35 0.32 -46.67 -70.98 83.35 0.32 -46.65 -69.41 86.33 0.32 -46.65 -69.41 86.33 0.32 -50.90 -76.95 87.46 0.20 -50.90 -76.75 87.46 0.20 -50.90 -76.76 87.72 0.32 -50.64 -75.88 83.99 0.33 -50.92 -75.48 93.98 17idecane 0.10 -54.96 -82.66 89.48 0.20 -55.12 -82.92 93.49 0.25 -55.18 -81.54 101.37 104 -59.34 -88.57 95.64 0.20 -59.34 -88.54 99.13 <		0.20	-70.76	-105.03	121.05
0.32-70.37-103.60116.890.53-70.38-102.27108.92Undecane0.10-46.61-70.9878.660.20-46.72-71.1383.360.25-46.70-70.9883.350.32-46.65-69.4186.330.53-46.65-69.4186.330.00-59.15-88.5795.640.20-50.90-76.9587.460.21-50.64-75.8883.590.22-50.64-75.8883.5917 idecane0.10-54.96-82.6689.480.53-50.92-75.4893.9817 idecane0.10-55.12-82.6393.010.25-55.05-82.6393.010.26-55.12-82.6393.0117 idecane0.10-59.15-85.7595.640.22-55.05-82.6393.010.32-55.18-81.54101.3717 idecane0.10-59.15-88.5795.640.25-55.05-82.6393.010.25-55.05-82.6393.010.26-55.18-81.54101.3717 idecane0.10-59.15-88.5795.640.20-59.34-88.8999.630.25-59.25-88.5499.130.26-59.24-87.7395.550.27-59.04-87.7395.550.28-59.04-87.55108.22 <td></td> <td>0.25</td> <td>-70.75</td> <td>-104.85</td> <td>122.57</td>		0.25	-70.75	-104.85	122.57
0.53-70.38-102.27108.92Undecane0.10-46.61-70.9878.660.20-46.72-71.1383.360.25-46.70-70.9883.350.32-46.65-69.4186.330.02-50.90-76.9587.460.25-50.90-76.9587.460.25-50.87-76.7687.720.32-50.64-75.8883.590.53-50.92-75.4893.98Tridecane0.10-54.96-82.6693.490.25-55.12-82.6693.490.26-55.18-81.54101.37Tridecane0.10-54.84-81.7890.190.32-55.18-81.54101.37Tetradecane0.10-59.15-88.5795.640.25-55.18-81.54101.370.53-59.24-88.8999.630.53-59.24-88.5795.640.20-59.34-88.8999.630.21-59.25-88.5499.130.22-59.04-87.7396.550.33-59.04-87.7396.550.53-59.04-87.7396.550.53-59.41-87.55108.22		0.32	-70.37	-103.60	116.89
Undecane 0.10 -46.61 -70.98 78.66 0.20 -46.72 -71.13 83.35 0.25 -46.70 -70.98 83.35 0.32 -46.65 -70.94 76.92 0.53 -46.65 -69.41 86.33 Dodecane 0.10 -59.15 -88.57 95.64 0.20 -50.90 -76.95 87.46 0.20 -50.87 -76.76 87.72 0.32 -50.64 -75.88 83.59 0.53 -50.92 -75.48 93.98 0.53 -50.92 -75.48 93.98 0.25 -55.05 -82.66 89.48 0.20 -55.12 -82.92 93.49 0.25 -55.05 -82.63 93.01 0.32 -55.18 -81.54 101.37 104 -59.15 -88.57 95.64 0.20 -59.34 -88.89 99.63 0.25 -59.25 -88.54 <		0.53	-70.38	-102.27	108.92
0.20 -46.72 -71.13 83.36 0.25 -46.70 -70.98 83.35 0.32 -46.46 -70.04 76.92 0.53 -46.65 -69.41 86.33 Dodecane 0.10 -59.15 -88.57 95.64 0.20 -50.90 -76.95 87.46 0.20 -50.87 -76.76 87.72 0.32 -50.64 -75.88 83.59 0.53 -50.92 -75.48 93.98 0.53 -50.50 -82.66 89.48 0.20 -55.12 -82.92 93.49 0.25 -55.05 -82.66 89.48 0.20 -55.12 -82.92 93.49 0.25 -55.05 -82.63 90.19 0.53 -55.18 -81.54 101.37 Tetradecane 0.10 -59.15 -88.57 95.64 0.20 -59.34 -88.89 99.63 0.25 -59.25 -88.54	Undecane	0.10	-46.61	-70.98	78.66
0.25-46.70-70.9883.350.32-46.46-70.0476.920.53-46.65-69.4186.33Dodecane0.10-59.15-88.5795.640.20-50.90-76.9587.460.25-50.87-76.7687.720.32-50.64-75.8883.59Tridecane0.53-50.92-75.4893.980.53-50.92-75.4893.490.20-55.12-82.9293.490.25-55.05-82.6393.010.25-55.05-82.6393.010.25-55.18-81.54101.37Tetradecane0.10-59.15-88.5795.640.20-59.15-88.5795.640.21-59.25-88.5499.630.22-59.04-87.7396.550.32-59.04-87.7396.550.53-59.41-87.55108.22		0.20	-46.72	-71.13	83.36
0.32-46.46-70.0476.920.53-46.65-69.4186.33Dodecane0.10-59.15-88.5795.640.20-50.90-76.9587.460.25-50.87-76.7687.720.32-50.64-75.8883.59Tridecane0.10-59.92-75.4893.980.53-50.92-75.4893.980.54-55.05-82.6689.480.25-55.05-82.6393.010.32-54.84-81.7890.190.53-55.18-81.54101.37Tetradecane0.10-59.15-88.5795.640.20-59.34-88.8999.630.53-59.25-88.5499.130.53-59.25-88.5499.130.53-59.41-87.73108.22		0.25	-46.70	-70.98	83.35
0.53-46.65-69.4186.33Dodecane0.10-59.15-88.5795.640.20-50.90-76.9587.460.25-50.87-76.7687.720.32-50.64-75.8883.59Tridecane0.10-54.96-82.6689.480.20-55.12-82.9293.930.21-55.05-82.6393.010.22-55.05-82.6393.010.23-55.18-81.54101.37Tetradecane0.10-59.15-88.5795.640.25-59.34-81.54101.370.25-59.34-88.5999.630.25-59.34-88.5795.640.25-59.34-88.5795.640.25-59.25-88.5499.130.32-59.41-87.7396.55		0.32	-46.46	-70.04	76.92
Dodecane 0.10 -59.15 -88.57 95.64 0.20 -50.90 -76.95 87.46 0.25 -50.87 -76.76 87.72 0.32 -50.64 -75.88 83.59 0.53 -50.92 -75.48 93.98 Tridecane 0.10 -54.96 -82.66 89.48 0.20 -55.12 -82.92 93.01 0.25 -55.05 -82.63 93.01 0.25 -55.18 -81.54 101.37 0.53 -59.43 -88.57 95.64 0.20 -59.15 -88.57 95.64 0.25 -59.25 -88.54 99.13 0.25 -59.25 -88.54 99.13 0.32 -59.04 -87.73 96.55 0.33 -59.41 -87.55 108.22		0.53	-46.65	-69.41	86.33
0.20 -50.90 -76.95 87.46 0.25 -50.87 -76.76 87.72 0.32 -50.64 -75.88 83.59 0.53 -50.92 -75.48 93.98 Tridecane 0.10 -54.96 -82.66 89.48 0.20 -55.12 -82.92 93.49 0.25 -55.05 -82.63 93.01 0.25 -55.18 -81.54 101.37 0.53 -55.18 -81.54 101.37 10.25 -59.25 -88.57 95.64 0.20 -59.34 -88.89 99.13 0.25 -59.04 -87.73 96.55 0.32 -59.04 -87.73 108.22	Dodecane	0.10	-59.15	-88.57	95.64
0.25 -50.87 -76.76 87.72 0.32 -50.64 -75.88 83.59 0.53 -50.92 -75.48 93.98 Tridecane 0.10 -54.96 -82.62 93.49 0.20 -55.12 -82.92 93.49 0.25 -55.05 -82.63 93.01 0.32 -55.18 -81.54 101.37 0.53 -55.18 -81.54 101.37 Tetradecane 0.10 -59.15 -88.57 95.64 0.20 -59.34 -88.59 99.63 0.25 -59.04 -87.73 96.55 0.32 -59.04 -87.73 108.22		0.20	-50.90	-76.95	87.46
0.32-50.64-75.8883.590.53-50.92-75.4893.98Tridecane0.10-54.96-82.6689.480.20-55.12-82.9293.490.25-55.05-82.6393.010.32-54.84-81.7890.190.53-55.18-81.54101.37Tetradecane0.10-59.15-88.5795.640.25-59.25-88.5799.630.25-59.25-88.5499.130.25-59.04-87.7396.550.32-59.04-87.73108.22		0.25	-50.87	-76.76	87.72
0.53-50.92-75.4893.98Tridecane0.10-54.96-82.6689.480.20-55.12-82.9293.010.25-55.05-82.6393.010.32-54.84-81.7890.190.53-55.18-81.54101.37Tetradecane0.10-59.15-88.5795.640.20-59.34-88.8999.630.25-59.25-88.5499.130.32-59.04-87.7396.550.53-59.41-87.55108.22		0.32	-50.64	-75.88	83.59
Tridecane 0.10 -54.96 -82.66 89.48 0.20 -55.12 -82.92 93.49 0.25 -55.05 -82.63 93.01 0.32 -54.84 -81.78 90.19 0.53 -55.18 -81.54 101.37 Tetradecane 0.10 -59.15 -88.57 95.64 0.20 -59.34 -88.89 99.63 0.25 -59.25 -88.54 99.13 0.32 -59.04 -87.73 96.55 0.53 -59.41 -87.55 108.22		0.53	-50.92	-75.48	93.98
0.20 -55.12 -82.92 93.49 0.25 -55.05 -82.63 93.01 0.32 -54.84 -81.78 90.19 0.53 -55.18 -81.54 101.37 Tetradecane 0.20 -59.34 -88.59 99.63 0.25 -59.25 -88.54 99.13 0.32 -59.04 -87.73 96.55 0.53 -59.41 -87.55 108.22	Tridecane	0.10	-54.96	-82.66	89.48
0.25 -55.05 -82.63 93.01 0.32 -54.84 -81.78 90.19 0.53 -55.18 -81.54 101.37 Tetradecane 0.10 -59.15 -88.57 95.64 0.20 -59.34 -88.89 99.13 0.32 -59.04 -87.73 96.55 0.53 -59.41 -87.55 108.22		0.20	-55.12	-82.92	93.49
0.32 -54.84 -81.78 90.19 0.53 -55.18 -81.54 101.37 Tetradecane 0.10 -59.15 -88.57 95.64 0.20 -59.34 -88.89 99.63 0.25 -59.25 -88.54 99.13 0.32 -59.04 -87.73 96.55 0.53 -59.41 -87.55 108.22		0.25	-55.05	-82.63	93.01
0.53 -55.18 -81.54 101.37 Tetradecane 0.10 -59.15 -88.57 95.64 0.20 -59.34 -88.89 99.63 0.25 -59.25 -88.54 99.13 0.32 -59.04 -87.73 96.55 0.53 -59.41 -87.55 108.22		0.32	-54.84	-81.78	90.19
Tetradecane 0.10 -59.15 -88.57 95.64 0.20 -59.34 -88.89 99.63 0.25 -59.25 -88.54 99.13 0.32 -59.04 -87.73 96.55 0.53 -59.41 -87.55 108.22		0.53	-55.18	-81.54	101.37
0.20-59.34-88.8999.630.25-59.25-88.5499.130.32-59.04-87.7396.550.53-59.41-87.55108.22	Tetradecane	0.10	-59.15	-88.57	95.64
0.25-59.25-88.5499.130.32-59.04-87.7396.550.53-59.41-87.55108.22		0.20	-59.34	-88.89	99.63
0.32-59.04-87.7396.550.53-59.41-87.55108.22		0.25	-59.25	-88.54	99.13
0.53 –59.41 –87.55 108.22		0.32	-59.04	-87.73	96.55
		0.53	-59.41	-87.55	108.22

value at a confidence interval of 99.9% are indicated in Table 3 by an asterisk. The number of degrees of freedom for each comparison depended on the number of data points used to construct each curve, which varied among the analytes, phases, and carrier gases. Hence, this value is indicated for each comparison in Table 3. As the critical value of *t* decreases with increasing degrees of freedom, the critical value of *t* indicated in Table 3 (3.883) is that for the lowest number of degrees of freedom (19) at a 99.9% confidence interval.

To evaluate the practical implications of these deviations, calculations of the root mean square error of prediction (RMSEP) in isothermal retention time were made for each compound across a range of temperatures. The results of these calculations are presented in Table 4 for the same analytes listed in Tables 2 and 3. These results indicated that a significant error was introduced by using thermodynamic parameters that did not correspond to the carrier gas being used to perform the separation. Moreover, the magnitude of the effect is difficult to predict. The average RMSEP for the compounds highlighted in Table 4 was found to be <1 s when considering predictions made for retention times in helium. For He against H₂ carrier gas there was a slight increase in the RMSEP; however, for most of the analytes investigated the deviations observed between the actual and predicted retention time were still small enough that they would be of little importance for all but the most demanding of modeling applications. The results for using He thermodynamics to make predictions in N₂ carrier gas on the other hand, showed a significant increase in the RMSEP in most cases, and in some showing an extreme increase in error. The magnitude of this error indicates a potential issue for applying thermodynamic models of retention time to separations that use nitrogen and likely air as a carrier gas. These types of systems are becoming increasingly popular for field-portable GC analyses. While mathematical models to aid in the identification of compounds based on retention time may not yet be included in such instruments as yet, the addition of such a capability is plausible, and the effects of carrier gas on the retention time predictions should be considered.

3.2. Investigation of a potential kinetic effect

As the thermodynamic parameters that are calculated are based upon measurements performed on a dynamic system, it is possible that a kinetic effect influencing mass transport could confound the results of this study. It is plausible that when the carrier gas is changed, the changes in viscosity and diffusion coefficients for molecules in the gas phase could result in the molecule experiencing a different diameter in terms of time required to reach the column wall (a change in the resistance to mass transport in the mobile phase term (C_m) of the van Deemter Equation). This could in turn alter the effective phase ratio and consequently the thermodynamic parameters extracted from the data.

To investigate this possibility, a series of columns having identical nominal phase ratios and phase chemistries but different diameters were purchased. If a kinetic effect was impacting the estimation of thermodynamic parameters, the values calculated for the parameters should change in a predictable manner across this series of columns. A series of n-alkanes and the analogous alcohols were separated on each of the five columns with different diameters. The three thermodynamic parameters ΔH , ΔS , and ΔC_p were collected in an identical manner to the aforementioned carrier gas studies. In reviewing the data for each of the thermodynamic parameters vs. column diameter for each of the compounds no correlation was apparent. Table 5 compares the thermodynamic parameters ΔH , ΔS , and ΔC_p against column inner diameter for several alkanes and alcohols. It is most likely that the precision with which we are able to estimate thermodynamic parameters is sufficiently high that the small differences between the nominal phase ratio provided by the manufacturer and actual phase ratio of the column, which will vary due to imperfections in column diameter and film thickness, are responsible for the observed variability.

4. Conclusions

The results of this study clearly show that the carrier gas used for a GC separation has an effect on the thermodynamics of the separation process. Furthermore, there is no obvious relationship between the observed changes in the thermodynamic parameters governing a separation when the carrier gas is changed and the structures of the molecules investigated. As yet, there is no correction factor that can be applied to account for the observed variations in the thermodynamics that would allow, for example, thermodynamic parameters derived in helium carrier gas to be used to make accurate predictions in other carrier gases. The possibility that a kinetic effect was influencing the results of the thermodynamic study was also investigated; however, based on our findings this is not likely. Our results demonstrate that when a model is constructed using data obtained in one carrier gas and applied in a system using a different carrier gas, there will almost certainly be some errors introduced into the predictions. Ultimately, the impact of this reduced accuracy depends on the requirements of the analyst, and for some molecules on some stationary phases the errors will be insignificant. However, for other molecules and phases there will be substantial errors observed. For the most precise research, it will be necessary to have thermodynamic data collected with a specific carrier gas in mind.

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