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Reversed-phase retention thermodynamics of pure-water mobile phases at ambient and elevated temperature

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Abstract

The use of pure water at superheated temperatures, between 100 and 200 °C, as a mobile phase for reversed-phase separations is explored. The thermodynamics of the retention process at low temperature (15–55 °C) are compared to the thermodynamics at elevated temperature (125–175 °C). Significant differences in the enthalpy of the retention process are observed between the two temperature ranges. This is possibly due to changes in the hydrogen-bond network of the pure-water mobile phase, which would change the solvation, and therefore retention, of non-polar solutes. The change in thermodynamic values between the two temperature regions invalidates extrapolation of retention as a function of temperature between the two temperature regions for the prediction of room-temperature pure-water retention factors. The thermodynamic changes observed as the temperature is increased are similar to those seen when mobile phase composition is changed (by adding organic modifier) at constant temperature.

Keywords: Retention; Thermodynamic parameters; Mobile phase composition; Temperature effects; Subcritical water chromatography; Superheated water chromatography; Water; Diethyl phthalate; Toluenes; Benzenes

1. Introduction

Reversed-phase liquid chromatography (RPLC) is the most widely-used liquid-phase separation technique. In general, a reversed-phase system consists of a non-polar stationary phase, typically an alkyl ligand bonded to a silica surface, and a polar mobile phase. The mobile phase is generally a mixture of water and an organic modifier such as methanol or acetonitrile. Ideally, pure water could be used as a reversed-phase mobile phase. However, at room temperature, water is too weak of an eluent for all but the most polar of solutes. For this reason, organic modifiers are used to increase the elution strength of the mobile phase.

There are two methods that can be used to decrease retention with pure-water mobile phases. Since the retention factor k' is the product of the partition coefficient K and the volume phase ratio ϕ, retention can be reduced by reducing either K or ϕ. Separations using room-temperature water as a mobile phase with chromatographic systems with a very low phase ratio have been reported [1]. This was accomplished by using a non-porous stationary phase, which greatly reduces the volume of the bonded stationary phase, and thus the phase ratio.

A second approach to reduce k' is to reduce K. This can be done by increasing the temperature of the system. Typically, in reversed-phase chromatography, the nature of the bonded phase and the composition of the mobile phase are the variables used to adjust retention. However, it has been shown that retention can change with temperature by as much as 5%/°C. Initially, this fact was used to demonstrate the need for keeping temperature constant for run-to-run reproducibility [2,3]. Recently, however, temperature has been used as a variable in the separation process [4–6].

Several workers have demonstrated the use of superheated water—that is, water between 100 and 200 °C, as a mobile phase for reversed-phase separations. As the temperature of water is increased, particularly above its room-temperature boiling point, the dielectric constant (which is a measure of polarity) decreases [7,8]. At 225 °C, water has a dielectric constant comparable to that of neat acetonitrile. At higher temperature, the solubility of non-polar solutes is greatly increased [9,10]. Based on this observation, it is

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reasonable to assume that superheated water could be used as a reversed-phase eluent, and solvent strength could be adjusted by changing temperature. Several reports on the utility of superheated water as a mobile phase have been presented [9–22], and a review of superheated water chromatography has recently been published [23].

Solvatochromic studies on superheated water also indicate that it should be useful as a reversed-phase mobile phase. The $E_T(30)$ polarity values of superheated water decrease with temperature, and around 225 °C, reach a value of around 55 kJ/mol [24]. This is consistent with a hydro-organic mobile phase with around 90% acetonitrile. There is an approximately linear change in polarity with temperature, suggesting that temperature could be used as a solvent-strength variable. The solvatochromic properties of superheated water have been further broken down into contributions for dipolarity/polarizability (π^*), and hydrogen bond donor (acidity, α) and acceptor (basicity, β) strength. At superheated water temperatures, the π^* value decreases, which is another indicator of a decrease in polarity. There is a significant decrease in the α value, which indicates a reduction in the extent of hydrogen bonding in the system. An increase in the β value is also observed [24], which coupled with the change in α suggests a disruption of the hydrogen-bond network in the water. A disruption in the hydrogen-bond network of water increases the solubility of non-polar solutes; this is because the hydrogen-bond network is the driving force for hydrophobicity in a system with non-polar solute and water as a solvent [25]. Chromatographically, the implication is an increase in reversed-phase solvent strength.

Pawlowski and Poole performed a solvatochromic study of superheated water chromatography [26], using a variety of test solutes on a polymer-based stationary phase. Their results also indicate a reduction in hydrogen bonding in the mobile phase as temperature is raised. They compared the selectivity changes as a function of temperature to selectivity changes as a function of mobile phase composition in traditional reversed-phase chromatography. The observed selectivity changes were different, indicating that superheated water chromatography should be taken as a complimentary technique to traditional RPLC.

In addition to separation of mixtures for analytical purposes, the chromatography experiment can be used to determine the thermodynamics of the retention process. The value of the pure-water retention factor, k'_w, has been shown to correlate well with the octanol–water partition coefficient. This number is the “standard measure” of hydrophobicity for a solute, and is often taken as an indicator of real-world partitioning processes, such as bioavailability and environmental transport. Ideally, a pure-water mobile phase could be used to determine an estimate for the octanol–water partition coefficient. However, as previously stated, pure-water mobile phases do not have the solvent strength to elute most solutes in a reasonable amount of time and with reasonable peak shape. To get around this problem, workers typically measure retention factors using a variety of hydro-organic mobile phases, and extrapolate the log of the retention factor to a pure-water mobile phase value. Unfortunately, there is no commonly-accepted model to use for mobile phase extrapolations. Plots of the logarithm of the retention factor versus mobile phase composition are typically non-linear, particularly in the region of low organic content in the mobile phase, and the degree and direction of curvature are both solute and mobile phase dependent [27,28].

The use of superheated water requires a few modifications of traditional HPLC instrumentation. A moderate amount of backpressure needs to be applied to the chromatographic system in order to prevent the mobile phase from boiling on-column. The vapor pressure of water at 200 °C is approximately 15 bar, so a fixed backpressure of 30–40 bar is typically used. Even at superheated temperatures (up to approximately 225 °C) water is nearly incompressible, so maintaining an exact, constant pressure is not necessary. All that is required is that enough pressure is applied to keep water in the liquid state. The backpressure regulator or restrictor is typically placed downstream of the detector (for UV-Vis detection), so the operator needs to be sure that the detector flow cell is able to withstand elevated pressure.

A second instrumental modification is a means of heating the analytical column and mobile phase. It is important that the mobile phase is heated to the same temperature as the column, or thermal mismatch band broadening may result [21,22,29–31]. This can be done by placing both the column and a preheating coil in an oil bath or oven. The preheating coil needs to be long enough to adequately heat the mobile phase before it reaches the column inlet.

Once the mobile phase stream leaves the column, it needs to be cooled before reaching the detector. In our laboratory, we have used mobile phases up to 80 °C without pre-detector cooling with no problem, however, for temperatures in the superheated water range, the mobile phase should be cooled at least somewhat to prevent damage to the detector. The can be done by adding a heat exchanger to the detector inlet, or by running the tube between the column and detector through a cool water bath. Fig. 1 shows a typical instrumental setup for use with superheated water chromatography.

Column stability is another issue when superheated water is used as a mobile phase. The most common stationary phases in reversed-phase chromatography are alkyl modified silicas. However, these are not recommended for use above 50–80 °C, depending on the silica and ligand type. At higher temperatures, the stationary phase can degrade from hydrolysis of the bonded ligands, or by dissolution of the base silica. There have been reports that ODS columns are stable, at least for a few thousand column volumes of eluent, with water mobile phases up to 100 °C [19], but this is still well below the range typically used for superheated water chromatography. For this reason, other non-silica phases such as zirconia [12,20,21] or polymer-based phases [11,14,15] are commonly used for superheated water chromatography. The retention and selectivity of these phases are slightly different

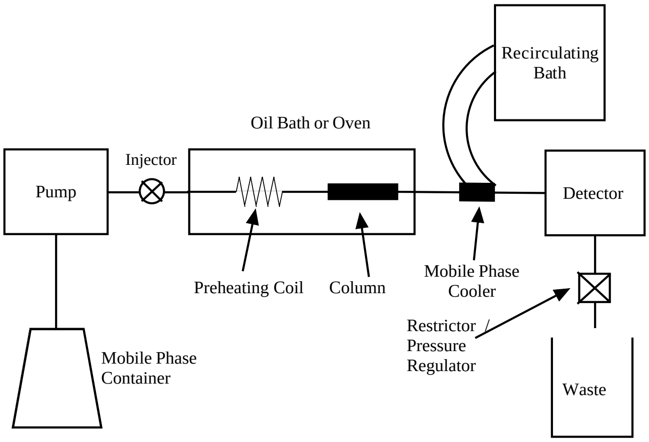

Fig. 1. A block diagram of an instrument for superheated water chromatography. The column heater and preheating coil, post-column mobile phase cooling apparatus, and pressure regulator are added to typical HPLC instrumentation to perform superheated water chromatography.

than what is seen with ODS, but the thermal stability of these phases dictates their use.

Since the polarity of superheated water varies with temperature, and is similar to the values observed for the hydro-organic mixtures commonly used in RPLC, it seems reasonable to assume that extrapolation of temperature, rather than mobile phase composition, could be used to determine room-temperature pure-water retention data. In this study, a variety of solutes were chromatographed using a variety of mobile phase compositions and temperatures, and comparisons of the extrapolation to a pure-water room-temperature retention factor are made. In addition, van't Hoff analysis is used to examine the enthalpy of retention with pure-water mobile phases. The retention thermodynamics of pure-water chromatography systems at both room and superheated temperature are compared to the thermodynamics of reversed-phase chromatography with hydro-organic mobile phases.

2. Experimental

2.1. Reagents

Water was purified to a resistance of 18 MΩ/cm, using a Barnstead (Debuque, IA, USA) water purification system. HPLC-grade acetonitrile was obtained from Fisher (Pittsburgh, PA, USA). Test solutes were diethyl phthalate, toluene, ethylbenzene, 4-chlorotoluene, and 1,2-dichlorobenzene, obtained from Aldrich (Milwaukee, WI, USA). Deuterated water (^2H_2O) was obtained from Cambridge Isotope Labs (Andover, MA, USA) for use as a void time marker. Silicone oil, for use in the oil heating bath, was also obtained from Fisher. All test solutions were made up in HPLC-grade acetonitrile. Mixed mobile phases were prepared by mixing measured volumes of water and acetonitrile.

2.2. Instrumentation

All experiments were performed on a Shimadzu (Kyoto, Japan) HPLC system. This system consisted of a model LC-10ADvp pump, a DGU-14A degasser, a SIL-10A autosampler, a SPD-10Avp UV-Vis detector, and a SCL-10Avp system controller. An injection volume of 7.5 μl was used. Data were collected and analyzed using Shimadzu Class-VP software. A 50 mm × 4.6 mm, ZirChrom-PBD (Anoka, MN, USA) column was used in this study. The stationary phase consisted of 3 μm particle diameter, 300 Å pore diameter polybutadiene-coated zirconia. We initially attempted to use a silica-based column for this study, but found (not entirely unexpectedly) that it degraded rapidly with superheated water conditions. A Fisher Scientific model 9105 recirculating bath was used to regulate column temperature between 15 and 55 °C. The same recirculating bath was used to cool the mobile phase between the column and detector. A silicon oil bath on a Corning (Acton, MA, USA) model PC-320 hot plate was used to regulate column temperatures above 100 °C. Backpressure of approximately 35 bar (500 psi) was applied to the system by using a fixed restrictor at the detector outlet. The restrictor was constructed of approximately 8 cm of 75 μm inner diameter fused silica capillary. During superheated chromatography runs, a stainless steel preheating coil, 1.2 m in length and with an internal diameter of 0.25 mm, was placed in the oil bath between the injector and the column. For all retention measurements, the extracolumn volume was determined by replacing the column with a union and measuring the elution time of ^2H_2O. The extracolumn volume was subtracted from all observed measurements. Refer to Fig. 1 for a schematic of our instrument.

3. Results and discussion

3.1. Estimation of retention by extrapolation

The original impetus for this work was to investigate whether or not temperature extrapolations could be used to estimate pure-water retention factors at ambient (35 °C) temperature, and if these extrapolations were more accurate than mobile phase composition extrapolations commonly used. Because we were using a short, polymer-coated zirconia stationary phase, which is not quite as retentive as ODS, we were able to measure room-temperature retention factors with pure-water mobile phases to compare to extrapolated values. This gave us the ability to assess the accuracy of each extrapolation. Mobile phase extrapolations were performed at 35 °C for a composition range of 5–50% acetonitrile in water, and temperature extrapolations (with a pure-water mobile phases) were made for a range of about 125–175 °C. These extrapolations are shown in Figs. 2 and 3. These retention values were extrapolated to estimate a retention value with a pure-water mobile phase at 35 °C, and compared to the measured values. None of these

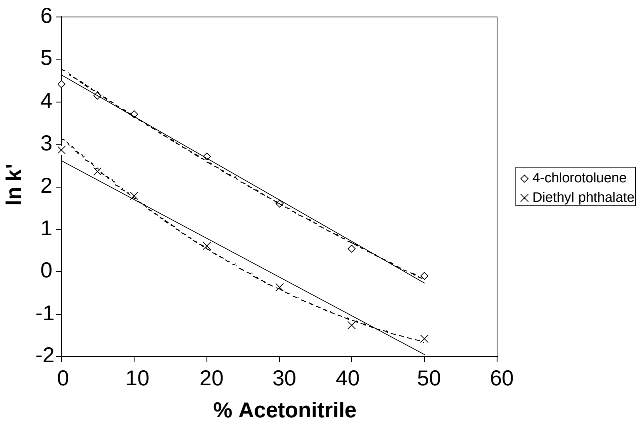

Fig. 2. Linear (solid line) and quadratic (dashed line) extrapolations of retention as a function of mobile phase composition. The data points at 0% acetonitrile are measured, and not included in the extrapolation.

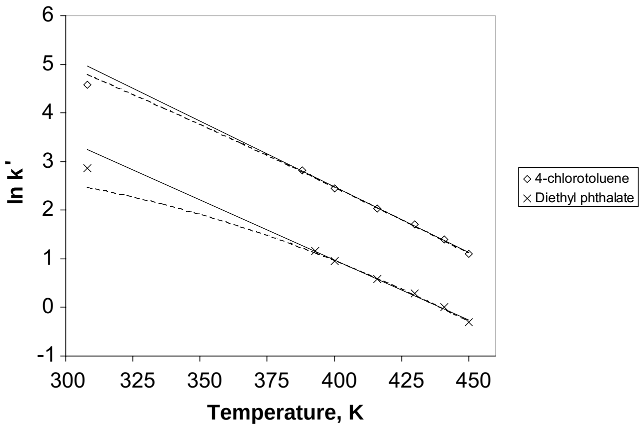

Fig. 3. Linear (solid line) and quadratic (dashed line) extrapolations of retention as a function of temperature. The data points at 35 °C are measured, and not included in the extrapolation.

extrapolations were able to consistently and accurately predict retention. The measured and extrapolated values are shown in Table 1 (mobile phase extrapolation) and Table 2 (temperature extrapolation).

3.2. *Thermodynamics of retention in superheated water*

Neither a linear or quadratic extrapolation of retention as a function of temperature has a rigorous thermodynamic basis. Both of these models were based on the empirical observation that the polarity of water decreases with an increase in temperature, much in the same way that the polarity of a hydro-organic mobile phase decreases in polarity with an increase in organic modifier content. A more thermodynamically-sound model for partitioning as a function of temperature is the van’t Hoff equation:

$$\ln K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{1}$$

where K is the partition coefficient of a solute between the two phases, ΔH° and ΔS° are the enthalpy and entropy change associated with the transfer of solute from one phase to another, R is the gas constant, and T is the temperature. Since the chromatographic retention factor k' is related to K via the volume phase ratio ϕ, which is the volume of the stationary phase divided by the volume of the mobile phase:

$$k' = K\phi \tag{2}$$

the van’t Hoff equation can be applied to chromatographic retention:

$$\ln k' = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} + \ln\phi \tag{3}$$

Thus, if the enthalpy, entropy, and phase ratio remain constant over the temperature range studied, $\ln k'$ should be a linear function of $1/T$. Alternatively, if the phase ratio is known, the enthalpy and entropy of solute transfer can be calculated

Table 1
Extrapolations of mobile phase percent organic to pure water for estimation of k'_w, and error associated with each model

Solute	Measured k'_w	Linear extrapolation to k'_w	Linear error (%)	Quadratic extrapolation to k'_w	Quadratic error (%)
Diethyl phthalate	17.5	13.7	21.9	20.5	17.1
1,2-Dichlorobenzene	89.0	111.4	25.3	135.9	52.7
4-Chlorotoluene	82.3	103.2	25.5	120.0	45.8
Ethylbenzene	50.2	66.4	32.4	70.5	40.6

Table 2
Extrapolation of retention using superheated water as a mobile phase to a temperature of 35 °C, and associated error

Solute	Measured k'_w	Linear extrapolation to k'_w	Linear error (%)	Quadratic extrapolation to k'_w	Quadratic error (%)
Diethyl phthalate	17.5	25.6	46.1	14.3	−18.6
Toluene	17.3	30.3	75.3	17.5	−0.1
Ethylbenzene	50.2	97.1	93.7	47.4	−5.6
1,2-Dichlorotoluene	89.0	139.4	56.7	110.0	23.6
4-Chlorotoluene	82.3	143.0	73.3	173.9	111.3

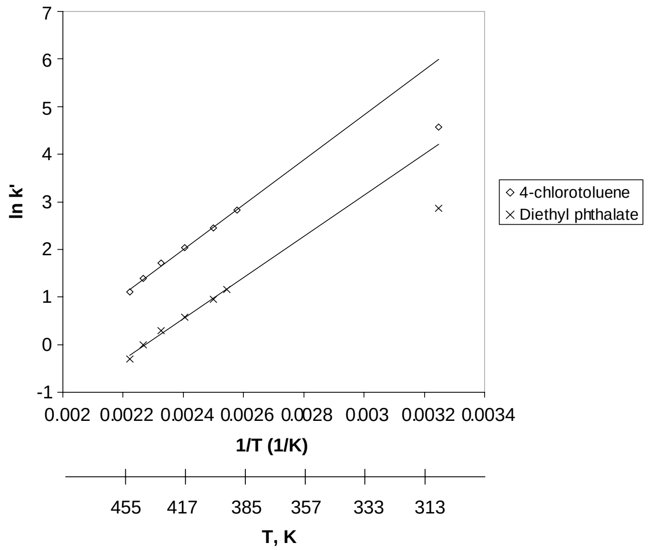

Fig. 4. van't Hoff extrapolation. A temperature axis is added for clarity. The data points at $1/T = 0.00325$ (308 K) are measured, and not included in the extrapolation.

from retention measurement over a range of temperatures. Conversely, if a van't Hoff plot is non-linear, that implies that either the thermodynamic values (enthalpy and entropy) and/or the phase ratio vary as a function of temperature [32].

Fig. 4 shows an extrapolation of $\ln k'$ versus $1/T$ to a value of $1/T$ corresponding to 35 °C (303 K). There is a significant amount of error in these extrapolations. The results of the van't Hoff extrapolations are shown in Table 3. For all solutes, error in the extrapolated versus measured values is at least 275%. This strongly suggests that the thermodynamics of the retention process are changing between ambient and superheated water temperatures.

van't Hoff analysis was used to measure the thermodynamics of the retention process with pure-water mobile phases at both ambient and superheated water temperatures. A low-temperature van't Hoff analysis was performed between 15 and 55 °C, and a high-temperature van't Hoff analysis was performed between 125 and 175 °C. Both sets of data were independently fit to the van't Hoff equation (Eq. (3)) Since the stationary phase volume of the column is unknown, we cannot calculate a phase ratio, so we are unable to calculate entropy values. However, we can get enthalpy values from the slopes of the van't Hoff plots. These values are shown in Table 4. A significant difference was observed between low-temperature and high-temperature enthalpies. In addition, the enthalpy of transfer of a methylene group, which is measured using a van't Hoff plot of the methylene selectivity, changes between the two different regions. Since selectivity van't Hoff plots are independent of phase ratio [32,33] this suggests that the observed van't Hoff plot curvature is due to changes in enthalpy, and not due to any possible changes in phase ratio. In order for the van't Hoff equation to hold as a model for extrapolation from superheated water temperature to 35 °C, these enthalpies need to be constant. Based on the significant difference in enthalpy between the low-temperature and high-temperature regions, it became apparent that there is a significant difference in the thermodynamics of retention between the two temperature regions. This precludes any extrapolation of superheated water retention data to room temperature.

Table 3
Extrapolation of retention using a superheated water mobile phase, based on a van't Hoff model

Solute	Estimated k'_w	Actual k'_w	Error (%)
Diethyl phthalate	67.7	17.5	286
Toluene	68.5	17.3	297
Ethylbenzene	250.3	50.2	399
1,2-Dichlorobenzene	388.7	89.0	337
4-Chlorotoluene	396.9	82.3	382

Table 4
Enthalpies of transfer of several test solutes at conventional temperatures (15–55 °C) and at superheated water temperatures (125–175 °C)

Solute	Low-temperature ΔH° (kJ/mol)	High-temperature ΔH° (kJ/mol)
Diethyl phthalate	−10.7	−36.0
Toluene	−5.7	−31.3
Ethylbenzene	−6.2	−36.3
1,2-Dichlorobenzene	−12.9	−39.3
4-Chlorotoluene	−11.5	−39.1
–CH_2 group	−0.6	−5.0

These results are not as surprising as they may seem when the solvent characteristics of superheated water are examined. Specifically, the hydrogen-bond network in water is significantly changed with an increase in temperature [25,34]. At extremely high temperatures, only monomeric water, that is, water with no hydrogen bonding is observed. As temperature is decreased, the extent of hydrogen bonding increases, especially below 200 °C [34]. This change in the hydrogen-bond structure of water should significantly change the thermodynamics of solvation of non-polar solutes, with a concomitant change in observed retention thermodynamics.

It may seem odd that the enthalpy of transfer (retention) at high temperature is more favorable than at low temperature, because retention is greater at low temperature. However, the thermodynamic quantity that governs retention is the free energy, which has an entropy component. Because of the change in the hydrogen-bond structure of water with temperature, the entropy change associated with retention changes with temperature. At lower temperatures, where the mobile phase is hydrogen bonded, there is a favorable entropy change upon retention. This is commonly referred to as the "hydrophobic effect" [35]. However, at high temperatures, where there is little or no hydrogen bonding, the entropy change would be expected to be much less. As a result, although the enthalpy of retention is more favorable at high temperature, it is outweighed by the entropic contribution. This has been observed before by Cole et al. [36]. They observed a change in enthalpy with temperature, with more favorable (more negative) enthalpies at higher temperatures. As the temperature decreased, the favorable entropy contribution increased, resulting in greater retention.

A similar changes in retention thermodynamics is seen when mobile phase composition, rather than temperature, is varied. In their study of the effect of temperature on retention in reversed-phase chromatography, Cole and Dorsey examined thermodynamic differences between hydrogen-bonded and non-hydrogen-bonded mobile phases [37,38]. It was shown that the thermodynamic signature was different depending on the hydrogen bonding of the mobile phase. At a given temperature, in a strongly hydrogen-bonded mobile phase (water or water–alcohol), retention was entropically driven. However, as the hydrogen-bond network is disrupted by the addition of a non-hydrogen-bonding organic modifier (in this case, acetonitrile), the retention becomes enthalpically driven. Similar results were observed by Wysocki [39]. This work was a thorough examination of the thermodynamics of retention as a function of mobile phase composition. As in the previous work of Cole and Dorsey, mobile phases with a high water content resulted in retention that was entropically driven. As the organic content of the mobile phase increased, retention became enthalpically driven. These results can be correlated to our work using temperature as a variable. As temperature is increased, the hydrogen-bond network of water is disrupted, similar to what occurs when organic modifier is added to water at room temperature. Thermodynamically, as the hydrogen-bond network is disrupted, either by an increase in temperature or an increase in the concentration of a non-hydrogen-bonding cosolvent, retention shifts from being entropically driven to enthalpically driven. The decrease in the dielectric constant of water as a function of temperature [7,8], as well as the shift in the $E_T(30)$ polarity value [24], also suggest a disruption of water's hydrogen-bond network at high temperature. The similarity between an increase in temperature of pure water and a change in composition of a mobile phase at constant temperature, coupled with the interesting solvatochromic properties of superheated water [26], suggest that superheated water chromatography would be a useful addition to the library of chromatographic techniques.

4. Conclusions

Based on our results, we conclude that extrapolation of retention data as a function of temperature should not be used to predict retention at a lower temperature, unless there is sufficient reason to believe that the thermodynamics of retention are constant between the measured and projected temperature regions. This does not appear to be the case when ambient (in the vicinity of 35 °C) and superheated water (above 100 °C) are used as the mobile phase. There appear to be significant differences in retention thermodynamics between the superheated water region and temperatures closer to ambient. The enthalpy of transfer from pure water to a non-polar stationary phase for small, non-polar solutes is much lower at ambient temperatures than at elevated temperatures. The change in thermodynamic values is most likely due to changes in the hydrogen-bond network in the water solvent. This changes the solvation structure around non-polar solutes, with a resultant change in retention thermodynamics. The thermodynamic changes are similar to those observed when organic modifier is added to a mobile phase at room temperature. Although superheated water is an interesting and potentially useful eluent for reversed-phase separations, retention with superheated water cannot be used to predict pure-water retention at room temperature because of the differences in retention thermodynamics at ambient and elevated temperature. Extrapolation of retention values as a function of temperature seem to have similar problems as extrapolation of retention as a function of mobile phase composition.

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