

INFLUENCE OF TEMPERATURE ON SPECIFIC RETENTION VOLUMES OF ENVIRONMENTALLY IMPORTANT VOLATILE ORGANIC COMPOUNDS IN GAS LIQUID CHROMATOGRAPHY

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ABSTRACT: Temperature dependence of specific retention volumes (V_g^o) of 13 volatile organic compounds (VOCs) of environmental importance between the gas and liquid stationary phase (polydimethylsiloxane, PDMS) are presented, determined by gas chromatographic method. Activity coefficients at infinite dilution were calculated from these specific retention volumes and they are in agreement with those obtained from static headspace and group contribution methods by the authors as well as literature values. The results of this work confirm that PDMS is well suited for VOCs scrubbing from waste gas streams. The measurements were carried out at temperatures (303.15, 313.15, 323.15., 333.15, 353.15, 373.15, 393.15 and 423.15) K to allow transport calculations for different seasons. Four PDMS polymers with average molecular weight ranging from 760 to 13 000

were used as solvents. Linear plots of $\log V_g$ against $\frac{1}{T}$ were obtained in all cases, thus allowing for predictions at other temperatures not investigated in this study. Since the typical van't Hoff plots were nicely linear, dependable enthalpies and entropies of solute transfer from the mobile phase to the stationary phase can also be calculated. Efforts were taken to ensure the best possible accuracy and trace the possible source of error. We devised a gas liquid chromatographic system which secured a simple retention mechanism and showed reproducible solute retention over a long period of time.

Key words: Specific retention volume, Waste gas streams, Stationary phase, Gas liquid chromatography, Scrubbing, Temperature dependence

INTRODUCTION

Solvents play a critical role in key chemical operations such as separation processes. Mostly known organic solvents such as polydimethylsiloxane contribute to solving air pollution problems due to their relatively high volatilities. For PDMS to be used effectively in the scrubbing of volatile organic compounds, it essential to know how they interact with different solutes. The important measure of this property is given by the specific retention volume (V_g^o) or the activity coefficient at

infinite dilution (γ_i^∞). Specific retention volumes can be used through the reduction of infinite dilution activity coefficients to design separation processes where the trace components or impurities have to be removed. The gas chromatography (GC) is suitable for measurement of specific retention volumes because of the negligible vapour pressure of PDMS. The procedure of the measurement in particular, the effect of flow rate of carrier gas, effect of sample size, and liquid loading were previously investigated (Muzenda et al. 2008, 2009)

The specific retention volume is defined as the net retention volume per gram of stationary phase at 0°C. This is very important because it allows the comparison of retention data obtained at different temperatures with different weight of stationary phase. Specific retention volumes were introduced by Littlewood et al. (1955). He suggested their use in place of partition coefficients in vapour identification. Littlewood measured specific retention volumes for a series of alcohols, aromatic hydrocarbons, and esters in silicone 702 – fluid and tritolyol phosphate. Lichtenthaler et al. (1973) measured specific retention volumes from gas – liquid chromatography for polydimethylsiloxane – hydrocarbon at 25, 40 and 55°C. The carrier gas flow rate was varied from 18 to 120 cm³ per minute and it was found to have no effect on the specific retention volumes. Summers, Tewari and Schreiber (1972) obtained specific retention volumes for polydimethylsiloxane – hydrocarbon systems in four columns with different liquid loading. Experimental temperature and flow rate were varied from 25 to 70°C and 70 to 120ml/min respectively. Ashworth and co – workers (1984) reported replicate gas – liquid chromatographic based specific retention volumes, activity coefficients and interaction parameters of ten solutes with polydimethylsiloxane at 303K.

Though inconclusive, the effects of temperature on retention data, in particular Kovats indices, has been investigated and debated for a long time (Heberger et al. 2002). Almost linear dependence of retention data for non polar solutes on non polar phases have been reported (Heberger et al. 2002). The Antoine type (which is non linear) shows better performance for wide temperature range for systems involving non polar solutes on polar stationary phases (Heberger et al. 2002). There have also been numerous studies of temperature effects on solute retention in reversed phase liquid chromatography (RPLC). Linear Van't Hoff plots were observed in the typical RPLC systems as reported and cited (Sentell et al. 1995). In these studies, the enthalpies of solute transfer from the mobile phase to the stationary phase were calculated from the slopes of the van't Hoff plots. Non linear plots are often observed when the temperature range is more than 45°C.

Usually the temperature dependency of the specific retention volume is expressed as

$$\ln V_g^0 = P \frac{1}{T} + Q \quad (1)$$

$$P = - \frac{\Delta H^s}{R} \quad (2)$$

$$Q = \ln \frac{273R}{M_s} + \frac{\Delta S^s}{R} \quad (3)$$

Where R is the universal gas constant M_s , is the molecular mass of the stationary phase. ΔH^s , ΔS^s are, respectively, the standard molar enthalpy and entropy of solution for the transfer of a mole of solute, from the ideal gas where its partial pressure is 1 atm, in the stationary phase, where its mole fraction is $\chi = 1$. The molecular interactions and the environment are similar to that of an infinitely dilute solution.

METHODOLOGY

The apparatus used has been described previously (Muzenda et al., 2000, 2002, 2008a, 2008b, 2009). The carrier gas was helium. A constant sample size of 0.1µl. was injected into the columns at constant flow rate of 35.97ml/min. Measurements were made at 303.15, 313.15, 323.15, 333.15, 353.15, 373.15, 393.15 and 423.15K. Special care was exercised to control and determine the system temperature accurately.

Column Preparation

Polydimethylsiloxane (PDMS) was coated into Chromosorb P, AW - DMCS or Chromosorb W, AW – DMCS (acid washed, dimethylchlorosiloxane treated) from a solution in chloroform. Details of column preparation are shown in Table 1.

Table 1: Description of columns

Properties	Column 1	Column 2	Column 3	Column 4
Length, m	1	1	1	1
Chromosorb W or P, g	6.158	7.291	7.186	4.86
PDMS, g	0.688	0.825	0.804	0.54
Wt % PDMS	10.05	10.16	10.06	10
Viscosity of PDMS, cp	5	10	50	500
Mw of PDMS	760	1000	3200	13000

MATERIALS

The materials used have been described previously (Muzenda et al., 2000, 2002, 2008a, 2008b, 2009). The thirteen solutes used in this work were coded numerically as in table 2 for simplicity.

Table 2: Solute Description and Code

Code no.	Compound	Code no.	Compound
1	chloroform	8	xylene
2	<i>n</i> -pentane	9	diethylether
3	<i>n</i> -hexane	10	butylacetate Isobutyl methyl ketone
4	<i>n</i> -heptane	11	ketone
5	acetone	12	triethylamine
6	toluene	13	ethylmethyl ketone
7	cyclohexane		

Calculations

The specific retention volume, corrected to 0°, is given by

$$V_g^o = \frac{3}{2} \left[\frac{\left(\frac{P_i}{P_o}\right)^2 - 1}{\left(\frac{P_i}{P_o}\right) - 1} \right] F(t_R - t_M) \frac{273.15}{W_s T_c} \quad (4)$$

In equation 4, F volumetric carrier gas flow rate at column outlet temperature and pressure, ml/min; $t_R - t_M$ is the retention time, ie., the time difference between air and solute peaks, min; T_c is column temperature, °K, W_s is weight of polymer in the column, g; P_i is inlet and P_o is outlet pressure. The use of the flame ionization detector permitted the application of the mathematical air peak method to approximate air peak maximum. To account for the gas holdup in the column, the retention time was taken as the difference between the maxima of the air and solute peaks (Purnell, 1962).

RESULTS AND DISCUSSION

Variation of specific retention volumes from literature findings

Table 3: Variation of specific retention volumes from literature findings

Compound	Temp (K)	Specific retention volumes			Source
		This work	Literature	% Variation	
chloroform	303	188.2	181.7	3.4	a
<i>n</i> -pentane	303	69.91	66.11	5.7	a
	313	47.81	47.65	0.3	a
	333	24.94	24.76	0.7	e
<i>n</i> -hexane	303	191.98	179.2	7.1	b
	313	126.23	124.2	1.6	d
	333	58.8	60.91	3.5	e
<i>n</i> -heptane	303	508.25	482.5	5.3	b
	313	294.57	290.8	1.3	c
	333	146.75	144.3	1.7	d
toluene	303	796.45	791.1	0.7	a
	313	529.08	516.6	2.4	b
	323	300.15	269.2	11.5	b
cyclohexane	303	336.8	315.1	6.9	b
	333	103.4	106	2.5	e
	303	2645.55	2654.6	0.3	c
xylene	313	1223.61	1187.5	3	b
	333	516.27	536.5	3.8	d

^aAshworth et al. (1984); ^bLichtenthaler et al. (1973); ^cDeshpande et al. (1974); ^dSmidsrod and Guillet (1969)

The solute specific retention volumes reported in Table 3 were calculated from corrected peak retention times using the well-known expression of Littlewood et al. (1955). The retention used in the calculation of specific retention volumes was an average of five measurements. Individual values of retention times were found to vary by no more than 1% in all cases. Specific retention volumes reported in this work compare very well with literature findings. The successful comparison gives an indication of the GLC as a rapid, simple and accurate method for studying the thermodynamics of the interaction of a volatile solute with a non volatile solvent. Therefore specific retention volumes obtained in this study can be considered to be accurate and reliable for the calculation of infinite dilution activity coefficients.

Temperature dependence of specific retention volumes

The specific retention volumes of chloroform, pentane, hexane, heptane, acetone, toluene, cyclohexane, xylene, diethyl ether, butyl acetate, isobutyl methyl ketone, triethylamine and ethyl methyl ketone were measured by injecting a constant amount of sample of 0.1 μ l into the four columns. Measurements were done at a constant mean flow rate of 35.97ml / min and the temperature was varied from 303.15 to 423.15K. Figures 1 to 4 show almost

linear dependence of $\log V_g$ on $\frac{1}{T}$ with V_g decreasing with increasing temperature. Chromatographic retention data from variable temperature runs may used to estimate thermodynamic properties according to the well-known Van't Hoff relation (Sellersgren and Shea, 1995).

$$\ln k' = -\Delta H / RT + \Delta S / R + \ln \phi \quad (5)$$

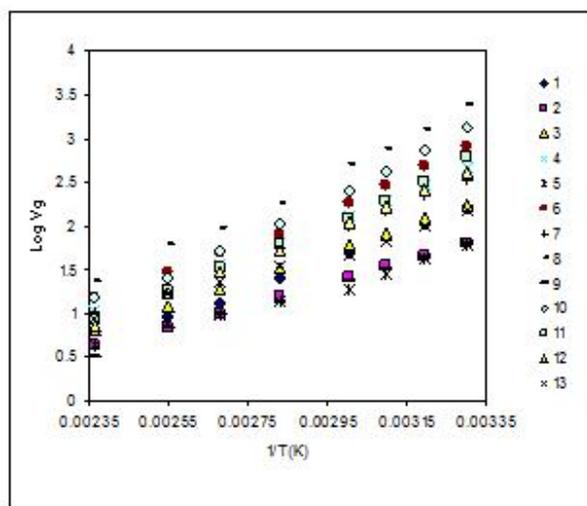


Figure 1: Effect T on Vg (Column 1)

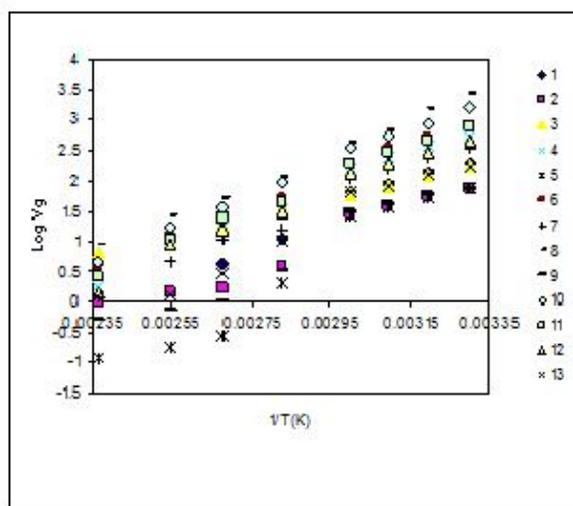


Figure 2: Effect of T on Vg (Column 2)

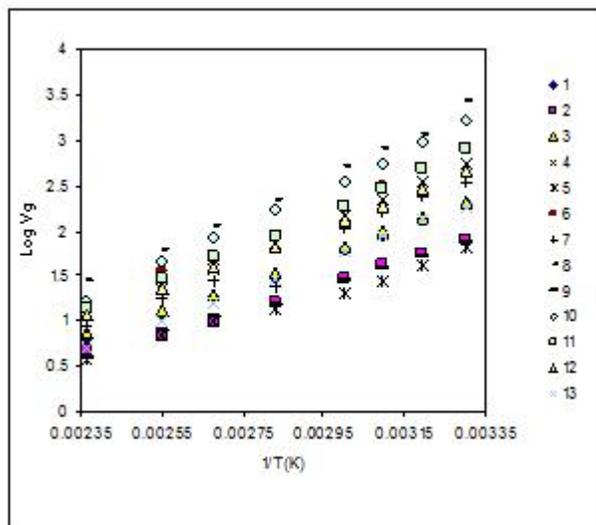


Figure 3: Effect of T on Vg (Column 3)

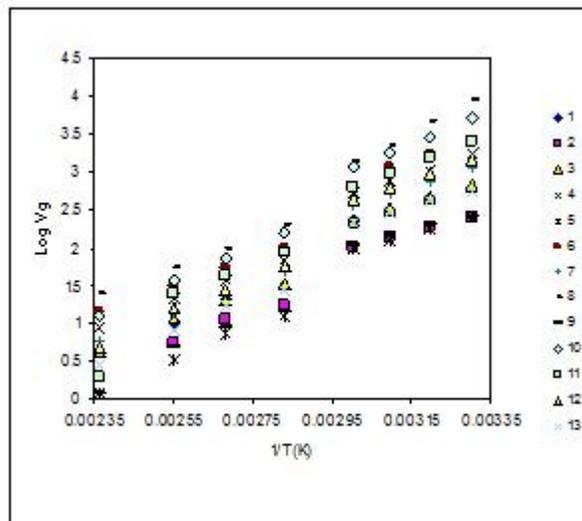


Figure 4: Effect of T on Vg (Column 4)

Where ϕ is the phase volume ratio and R is gas constant. The linear portions of these plots give enthalpies ($\Delta H/RT$) and entropies (ΔS) for the transfer of one mole of solute into the stationary phase. All the Van't Hoff plots obtained in this study were linear, and the regression correlation coefficients were better than 0.999 in all cases. Typical Van't Hoff plots are shown in Figures 1 to 4. The trends obtained here are in agreement with those observed by Ulrich et al. (2006), Sellergren and Shea (1995), Domanska and Marciniak (2008), Tudor (1997), Tudor and Moldovan (1999), Lee and Cheong (1999), Makela and Pyy (1995) and Sentel et al. (1995).

The choice of optimum of temperature for the absorption process requires knowledge of temperature dependence of the activity coefficient. Infinite dilution calculated from the specific retention volumes shows that the higher the temperature the higher the activity coefficients. This tendency is very favourable for the desorption, because the higher values at higher temperature would ease regeneration.

CONCLUSION

Specific retention volumes for 13 volatile organic compounds in polydimethylsiloxane were measured over the temperature range from 303.15 K to 423.15K using the GLC method. Good linear relationships were observed on the plots of $\log V_g$ versus ϕ . This can be used to predict the specific retention volumes and hence infinite dilution activity coefficients at temperatures not studied here. The measurements were highly reproducible with relative standard deviation and coefficient of variation in the determination of specific retention volumes of 0.00013 and 0.013 respectively. The control of the operating conditions as indicated by the stability of the baseline and the shapes of the peaks indicated that the equipment was working properly. The close agreement of the specific retention volumes and infinite dilution activity coefficients calculated from this study with those reported in literature proved that a sound technique was used.

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