

Temperature Effect on Volatile Organic Compounds – Polydimethylsiloxane Interactions

Edison Muzenda and Freeman Ntuli

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) were studied using the gas liquid chromatographic technique (GLC). Temperature was varied from 303.15K to 423.15K to allow transport calculations for different seasons. Four PDMS polymers with average molecular weight ranging from 760 to 13 000 were used as solvents. The results of this work confirm that PDMS is well suited for VOCs scrubbing from waste gas

streams. Linear plots of $\log V_g^o$ against $\frac{1}{T}$ were obtained in all cases permitting predictions and interpolations to temperatures not studied here. Also dependable enthalpies and entropies of solute transfer from the mobile phase to the stationary phase can be calculated. The specific retention volumes reported in this work are in agreement with literature for similar systems. Efforts were taken to ensure the best possible accuracy and trace the possible sources of error. A gas liquid chromatographic system which secured a simple retention mechanism and showed reproducible solute retention over a long period of time was devised.

Index Terms—Environmental, scrubbing, specific retention volume, stationary phase, waste gas streams

I. INTRODUCTION

The interaction between volatile organic compounds and polydimethylsiloxane in the form of specific retention volumes (V_g^o) at varying temperatures is presented in this study. Many polymeric solvents such as polydimethylsiloxane (PDMS) may play critical roles in the absorption of volatile organic compounds from contaminated air streams. In order to effectively use PDMS in the scrubbing of volatile organic compounds it essential to know how they interact with these compounds. 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 GLC is suitable for

measuring specific retention volumes because of the small 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 [1, 2].

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 [3]. Reference [3] suggested their use in place of partition coefficients in vapour identification. Reference [3] measured specific retention volumes for a series of alcohols, aromatic hydrocarbons, and esters in silicone 702 – fluid and tritolyl phosphate. Reference [4] measured specific retention volumes using GLC for polydimethylsiloxane – hydrocarbon systems at 298, 313 and 328K. 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. Reference [5] obtained specific retention volumes for polydimethylsiloxane – hydrocarbon systems in four columns with different liquid loading. Experimental temperature and flow rate were varied from 298 – 343K and 70 to 120ml/min respectively. Reference [6] 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 have been investigated and debated for a long time [7]. Almost linear dependence of retention data for non-polar solutes on non-polar phases have been reported [7]. The Antoine type (which is nonlinear) shows better performance for wide temperature range for systems involving non polar solutes on polar stationary phases [7]. 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 [8]. In these studies the enthalpies of solute transfer from the mobile phase to the stationary phase were calculated from the van't Hoff plots. Nonlinear plots are often observed when the temperature range is more than 318K. Usually the temperature dependency of the specific retention volumes is expressed as

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

where

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

Manuscript received September 6, 2011; revised October 18, 2011.

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

where R is the universal gas constant, M_s is the molecular mass of the stationary phase. ΔH^s and 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 $x = 1$. The molecular interactions and the environment are similar to that of an infinitely dilute solution.

II. METHODOLOGY

The apparatus used have been described previously [1], [2], [9]-[11]. The carrier gas was helium. A constant sample size of $0.1 \mu\text{l}$ was injected into the columns at constant flow rate of 35.97ml/min. Measurements were made at temperatures varying from 303.15K to 423.15K. Special care was exercised to control and determine the system temperature accurately.

A. Materials

The materials used have been described previously [1], [2], [9] - [11]. The thirteen solutes used in this work were coded numerically as in TABLE II for simplicity.

TABLE II: 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
4	<i>n</i> -heptane	11	Isobutyl methyl ketone
5	acetone	12	triethylamine
6	toluene	13	ethyl methyl ketone
7	cyclohexane		

B. 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 I: 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

C. Calculations

The primary GLC data are the retention time, which is the time taken by the component to traverse through the column

and the retention volume V_R , the volume of carrier gas passing through that time. The net retention volume V_N , is defined as in (4), where V_{gas} is the volume of gas in the column (gas hold-up). The gas hold up volume is a measure of total volume of space available to the mobile phase in the system, that is the column dead volume, injector and detector volumes and volumes of any connecting tubing for example from column to detector. In a well designed system, the extra dead volume is small compared to the column void volume.

$$V_N = V_R - V_{gas} \quad (4)$$

In gas-liquid columns the gas hold-up contributes 1 to 10 percent of the total retention volume. The homologous series method was used in this work because of the sensitivity of the flame ionization detector at low concentrations of the organic compounds. The time the non sorbed molecule takes to traverse through the column is given as in (5)

$$t_M = \frac{t_{R_1} t_{R_3} - t_{R_2}^2}{t_{R_1} + t_{R_3} - 2t_{R_2}} \quad (5)$$

The retention time t_R is made up of t_M , the time the solute spends in the mobile phase and t_s , the time the solute spends in the stationary phase. Separations are due to different times solutes spend in the stationary phase. The adjusted retention volume is given by (6).

$$V_R' = F_o t_R' = V_R - V_M \quad (6)$$

The corrected retention volume, V_R^o which takes into account the compressibility of the gaseous mobile phase, is given in (7).

$$V_R^o = j_3^2 V_R \quad (7)$$

The factor j_3^2 (7) corrects for the influence of pressure along the column and is given in (8).

$$j_3^2 = \frac{3}{2} \frac{\left[\left(\frac{p_i}{p_o} \right)^2 - 1 \right]}{\left[\left(\frac{p_i}{p_o} \right)^3 - 1 \right]} \quad (8)$$

The relationship between the net retention volume V_N and the carrier gas flow rate at the column outlet F_o and the retention times t_R and t_M for absorbed solute and carrier gas respectively is given in (9).

$$V_N = j_3^2 F_o (t_R - t_M) \quad (9)$$

The specific retention volume, corrected to 0° , is given in (10).

$$V_g^o = \frac{273.15 V_N}{W_s T_c} \quad (10)$$

In (7-10), j_3^2 is the gas compressibility factor, F_o is volumetric carrier gas flow rate at column outlet temperature and pressure, ml/min; $t_R - t_M$ is the retention time, i.e., 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 and p_o are inlet and outlet pressures respectively. 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 [12].

III. RESULTS AND DISCUSSION

A. Variation of Specific Retention Volumes from Literature Findings

The solute specific retention volumes reported in Table 3 were calculated from corrected peak retention times using the well known expression of [3]. The retention times used in the calculation of specific retention volumes were averages 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 nonvolatile solvent.

TABLE III: VARIATION OF SPECIFIC RETENTION VOLUMES FROM LITERATURE FINDINGS (PDMS MW \approx 3200)

Code	Temp (K)	Specific retention volumes			Source
		This work	Literature	% Variation	
1	303	188.2	181.7	3.4	[6]
	313	69.9	66.1	5.7	[6]
2	313	47.8	47.7	0.3	[6]
	333	24.9	24.8	0.7	[3]
	303	192.0	179.2	7.1	[6]
3	313	126.2	124.2	1.6	[14]
	333	58.8	60.9	3.5	[3]
	303	508.3	482.5	5.3	[4]
4	313	294.6	290.8	1.3	[14]
	333	146.8	144.3	1.7	[14]
	303	796.5	791.1	0.7	[6]
6	313	529.1	516.6	2.4	[4]
	323	300.2	269.2	11.5	[4]
	303	336.8	315.1	6.9	[4]
7	333	103.4	106.0	2.5	[3]
	303	2645.6	2654.6	0.3	[13]
	313	1223.6	1187.5	3.0	[4]
8	333	516.3	536.5	3.8	[14]

4.2 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 constant mean flow rate of 35.97ml / min and the temperature was varied from 303.15 to 423.15K. Chromatographic retention data from variable temperature runs may be used to estimate thermodynamic properties according to the well-known Van't Hoff relation [8] using (11).

$$\ln k' = -\Delta H / RT + \Delta S / R + \ln \phi \quad (11)$$

where ϕ is the phase volume ratio and R is the 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 similar to those observed by [8], [15] – [21].

The choice of the optimum temperature for the absorption process requires knowledge of temperature dependence of the activity coefficient. The derived Infinite dilution activity coefficients [2], [9] – [11] calculated from the specific retention volumes reported in this study show that the higher the temperature the higher the activity coefficients. This tendency is very favorable for desorption, because higher values at higher temperature would ease regeneration.

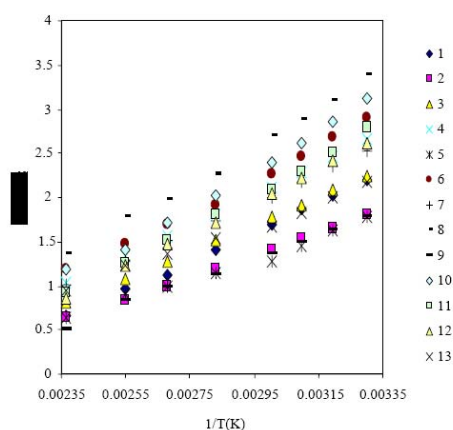


Fig. 1. Effect t on vg (column 1)

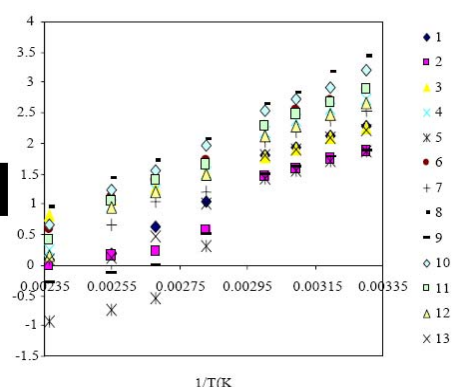


Fig. 2. Effect of t on vg (column 2)

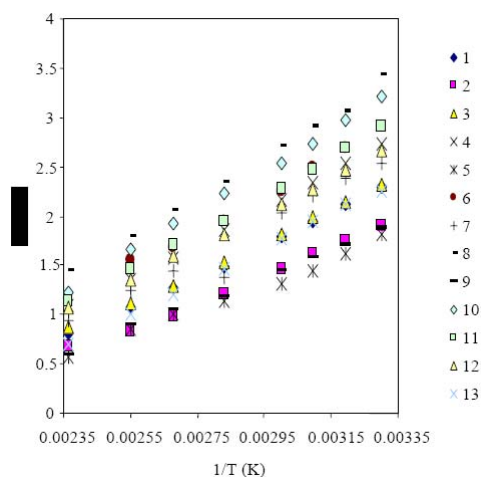


Fig. 3. Effect of t on v_g (column 3)

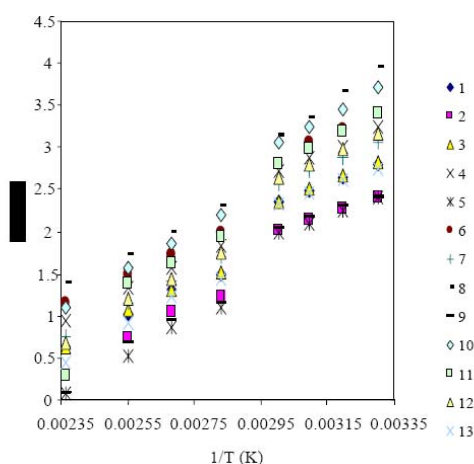


Fig. 4. Effect of t on v_g (column 4)

I. 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 gas liquid chromatographic technique. Good linear relationships were observed on the plots of $\log V_g$ versus $1/T$. This can be used to predict the specific retention volumes and hence infinite dilution activity coefficients at temperatures not considered in this study. 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 close agreement of the specific retention volumes obtained in this study with those reported in literature proved that a sound technique was developed.

NOMENCLATURE

- F_o - carrier gas flow rate (ml/min)
- ΔH^h - standard molar enthalpy ($Jmol^{-1}K^{-1}$)
- ΔH^s - standard molar entropy ($Jmol^{-1}mol^{-1}$)
- j_3^2 - gas compressibility factor
- M_2 - average polymer molecular weight (g/mol)

- M_s - molecular mass of stationary phase (g)
- n - normal
- p_i - inlet pressure (Pa)
- p_o - outlet pressure
- P_i^o - vapour pressure of solute, i
- R - universal gas constant ($JK^{-1}mol^{-1}$)
- T_c - column temperature
- t_M - retention time of air (min)
- t_R - retention time of solute
- V_g - specific retention volume (ml/g)
- V_N - net retention volume (ml)
- W_s - weight of stationary phase

GREEK LETTERS

- γ - activity coefficient

SUBSCRIPTS

- i - solute
- g - specific
- N - net
- R - retention

ACKNOWLEDGMENT

We are indebted to the Departments of Chemical Engineering of the University of Johannesburg. The encouragement and advice of Aubrey Arrowsmith is greatly appreciated.

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