

A Note on the Dependence of Volatile Organic Compounds Specific Retention Volumes on Temperature

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Abstract: This study investigated the influence of temperature on the specific retention volumes (V_g^o) of 13 volatile organic compounds (VOCs) in silicon oil as the liquid stationary phase using gas liquid chromatography (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. Linear plots of $\log V_g$ against $1/T$ were obtained in all cases permitting predictions and interpolations to temperatures not studied here and 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. We devised a gas liquid chromatographic system which secured a simple retention mechanism and showed reproducible solute retention over a long period of time.

Keywords: environmental, specific retention volume, temperature dependence, waste gas streams.

1. Introduction

Many polymeric solvents, such as silicon oil chemically known as polydimethylsiloxane (PDMS), 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 is 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^∞). 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. Though inconclusive, the effects of temperature on retention data in particular Kovats indices have been investigated and debated for a long time Heberger et al. [1]. Almost linear dependence of retention data for non polar solutes on non polar phases have been reported [1]. The Antoine type (which is non linear) shows better performance for wide temperature range for systems involving non polar solutes on polar stationary phases [1]. 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 [2]. Usually the temperature dependency of the specific retention volume is expressed as

$$\ln V_g^o = -\frac{\Delta H^s}{R} \frac{1}{T} + \ln \frac{273 R}{M_s} + \frac{\Delta S^s}{R} \quad (1)$$

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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.

2. Methodology

The apparatus used have been described previously [3, 4]. The carrier gas was helium. A constant sample size of $0.1 \mu l$ was injected into the columns at constant flow rate of 35.97ml/min at various temperatures. Special care was exercised to control and determine the system temperature accurately.

2.1 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

2.2 Materials

The materials used here have been described previously [3, 4]. 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
4	<i>n</i> -heptane	11	Isobutyl methyl ketone
5	acetone	12	triethylamine
6	toluene	13	ethyl lmethyl ketone
7	cyclohexane		

3. Calculations

The specific retention volumes volume, corrected to 0° , is given by equation 2, where, F 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, p_i is inlet and p_o is outlet pressure.

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

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 [5].

4. Results and Discussion

4.1 Variation of specific retention volumes from literature findings

Table 3: Variation of specific retention volumes from literature findings

Compound	Temp (K)	Specific retention volumes		% Variation	Source
		This work	Literature		
chloroform	303	188.2	181.7	3.4	[6]
<i>n</i> -pentane	303	69.91	66.11	5.7	[6]
	313	47.81	47.65	0.3	[6]
	333	24.94	24.76	0.7	[10]
	303	191.98	179.2	7.1	[7]
<i>n</i> -hexane	313	126.23	124.2	1.6	[9]
	333	58.8	60.91	3.5	[10]
	303	508.25	482.5	5.3	[7]
<i>n</i> -heptane	313	294.57	290.8	1.3	[8]
	333	146.75	144.3	1.7	[9]
	303	796.45	791.1	0.7	[6]
toluene	313	529.08	516.6	2.4	[7]
	323	300.15	269.2	11.5	[7]
	303	336.8	315.1	6.9	[7]
cyclohexane	333	103.4	106	2.5	[10]
	303	2645.55	2654.6	0.3	[8]
xylene	313	1223.61	1187.5	3	[7]
	333	516.27	536.5	3.8	[9]

The retention time 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.

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 studied. Figures 1 to 4 show almost linear dependence of $\log V_g$ on $1/T$ with V_g decreasing with increasing temperature. Chromatographic retention data from variable temperature runs may be used to estimate thermodynamic properties according to the well-known Van't Hoff relation (equation 5) [11].

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

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. The trends obtained here are similar to those observed [2, 11, 12, 13, 14, 15, 16, 17].

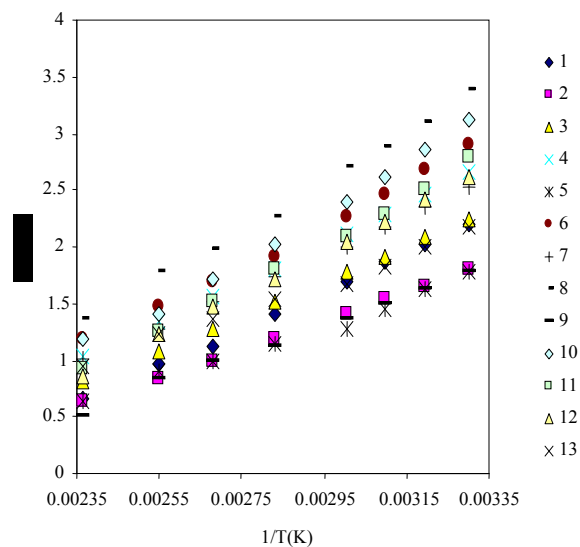


Fig. 1: Effect T on V_g (Column 1)

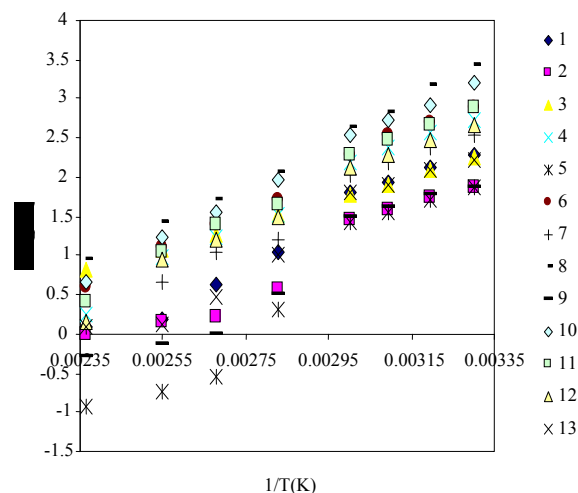


Fig. 2: Effect of T on V_g (Column 2)

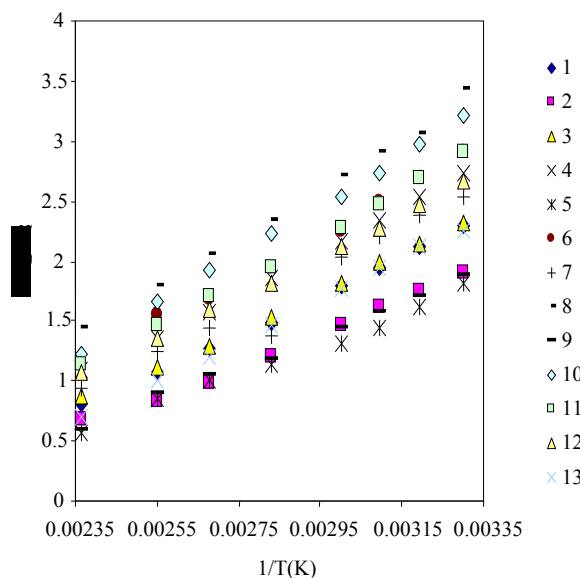


Fig. 3: Effect of T on V_g (Column 3)

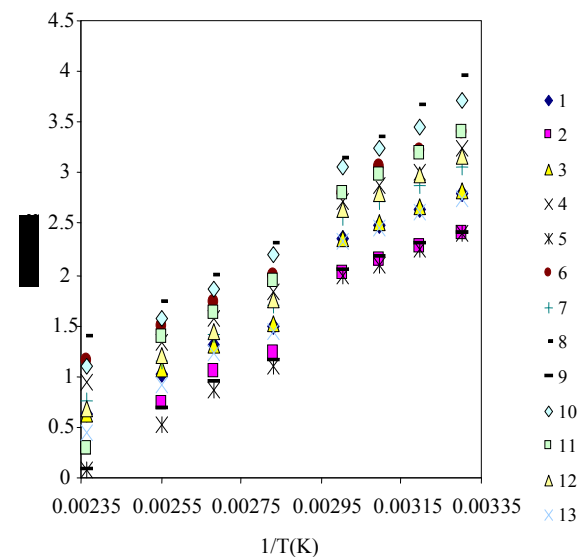


Fig. 4: Effect of T on V_g (Column 4)

5. Conclusions

Specific retention volumes for 13 volatile organic compounds in polydimethylsiloxane were measured over the temperature range 303.15 K to 423.15 K using the gas liquid chromatography. Good linear relationships were observed on the plots of $\log V_g$ versus $1/T$. 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.

6. Acknowledgements

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7. References

- [1] K. Heberger, M. Gorgenyi and T. Kowalska. Temperature dependence of Kovats indices in gas chromatography revisited. *J. Chrom. A.* 2002, 973, 135-142.
- [2] K.B. Sentell, N.I. Ryan and A.N. Henderson. Temperature and salvation effects on homologous series selectivity in reversed phase liquid chromatography. *Analy.Chimica Acta.* 1995, 307, 203-215.
- [3] E. Muzenda, M. Belaid, F. Ntuli and A. Arrowsmith. Absorption of Volatile Organic Compounds in Silicon: Determination of Infinite Dilution Activity Coefficients by Dynamic Gas Liquid Chromatographic Technique. Proc. of the 8th WCCE 2009, Montreal, Quebec, Canada: August 23-27, 2009.
- [4] E. Muzenda, M. Belaid and F. Ntuli. Measurement of Infinite Dilution Activity Coefficients of Selected Environmentally Important Volatile Organic Compounds in Polydimethylsiloxane using Gas – Liquid Chromatography. *Kor. J. Chem. Eng.* 2010, 27(5): 1509-1512.
- [5] H. Purnell. *Gas Chromatography.* John Wiley and Sons 1962.
- [6] A.J. Ashworth, C.F. Chien, D.L. Furio, D.M. Hooker, M.M. Kopecni, R.J. Laub and G.J. Price. Comparison of static with gas-chromatographic solute infinite-dilution activity coefficients with polydimethylsiloxane solvent. *Macromolecules*, 1984, 17(5): 1090-1094.
- [7] R.N. Lichtenthaler, R.D. Newman and J.M. Prausnitz. Specific retention volumes from Gas – Liquid Chromatography for Polydimethylsiloxane Hydrocarbon Systems. *Macromolecules*, 1973, 6(4): 650-651.
- [8] D.D. Deshpande, D. Patterson, H.P. Schreiber and S.C. Su. Thermodynamic Interactions in Polymer Systems by Gas – Liquid Chromatography. IV. Interactions between Components in a Mixed Stationary Phase. *Macromolecules*, 1974, 7(4): 530-535.
- [9] O. Smidsrod and J.E. Guillet. Study of polymer interactions by gas chromatography. *Mactomolecules*, 1969; 2, 272-275.
- [10] A.B. Littlewood, C.S.G. Phillips C.S.G. and D.T. Price. The Chromatography of gases and vapours Part V: Partition analysis with columns of Silicone 702 and Tritolyphosphate. *J. Chemical Soc.* 1955, 1480.
- [11] B. Sellergren and J.H. Shea. Origin of peak asymmetry and the effect of temperature on the solute retention in enantiomer separations on imprinted chiral stationary phases. *J. Chrom. A.* 1995, 690: 29 – 39.
- [12] K. Bay, H. Wanko and J. Ulrich. Absorption of Volatile Organic Compounds in Biodiesel: Determination of Infinite Dilution Activity Coefficients by Headspace Gas Chromatography. *ICHEM*. 2006, 84(A1): 22 – 28.
- [13] U. Domanska and A. Marciniak. Measurements of activity coefficients at infinite dilution of aromatic and aliphatic hydrocarbons, alcohols, and water in the new ionic liquid [EMIM][SCN] using GLC. *Journal of Chemical Thermodynamics*, 2008, 40: 860 – 866.
- [14] E. Tudor. Temperature dependence of the retention index for perfumery compounds on a SE – 30 glass capillary column I. Linear Equations. *J. Chroma. A.* 1997, 779: 287 – 297.
- [15] E. Tudor and D. Moldovan. Temperature dependence of the retention index for perfumery compounds on a SE – 30 glass capillary column II. The hyperbolic equation. *J. Chroma. A.* 1999, 848: 215 – 227.
- [16] C.S. Lee and W.J. Cheong. Thermodynamic properties for the solute transfer from the mobile to the stationary phase in reversed phase liquid chromatography obtained by squalane – impregnated C18 bonded phase. *J. Chroma. A.* 1999, 848: 9 – 20.
- [17] M. Makela and L. Pyy. Effect of temperature on the retention time reproducibility and on the use of programmable fluorescence detection of fifteen polycyclic aromatic hydrocarbons. *J. Chroma. A.* 1995, 699: 49 – 57.