

A Review of Polydimethylsiloxane – Volatile Organic Compounds Interactions

Edison Muzenda

Abstract—This paper is a review on the interactions of certain volatile organic compounds with polydimethylsiloxane using the gas liquid chromatographic technique (GLC). The interactions reviewed here were studied in the form of specific retention volumes. Only single stationary phases were considered in this review. For similar systems, the retention data agrees very well. This review has shown that the GLC is a rapid and convenient method to obtain thermodynamic data for polymeric systems. This work is very useful in the determination of phase equilibrium in form of infinite dilution activity coefficients necessary for the design of absorption and stripping columns for the abatement of volatile organic compounds from contaminated air streams.

Keywords—Chromatography, interactions, polydimethylsiloxane, polymers, specific retention volume, thermodynamics

I. INTRODUCTION

THE application of gas – liquid chromatography (GLC) to the determination of thermodynamic interactions in systems with a polymeric component as a stationary phase has been the subject of several investigations in the past 5 decades. A gas chromatographic column is usually filled with a solid support material which contains a layer of the stationary phase. The retention of a moving solute depends on the partition of the solute between the stationary phase and the mobile gas phase. This retention is governed by the saturation vapour pressure of the solute at the column temperature and the tendency of the stationary phase to sorb the solute molecule. When absorption in the bulk polymer is the dominant mechanism, the theory of gas liquid partition chromatography maybe applied to the results to calculate various thermodynamic quantities. This paper reviews the thermodynamic interactions involving volatile organic compounds with polydimethylsiloxane (PDMS) in the form of

specific retention volumes (V_s^o) . Polymeric solvents such as polydimethylsiloxane (PDMS) may play crucial roles in the absorption of volatile organic compounds (VOCs) 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 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 [1]. Reference [2] considered the application of gas – liquid chromatographic techniques to polymer solution thermodynamics. The primary interest was to determine thermodynamic quantities through this technique. This was prompted by comments from several researchers who noted the difficulty of applying the usual thermodynamics equations

of the G.L.C which yield γ_i^∞ , the activity coefficient of component 1 (VOC) at infinite dilution. This is because the equations require an exact molecular weight value of component 2, thus complicating their applicability to polymer systems. Their many objectives were to resolve this problem and they also stressed the utility of the technique in testing contemporary theories of polymer solution thermodynamics.

II. THE REVIEW

Reference [3] measured specific retention volumes using gas – liquid chromatography for polydimethylsiloxane - hydrocarbon systems as part of a more extensive study of polymer solvent interactions. The carrier gas was helium, measurements were performed at 25, 40 and 55°C. A lot of attention was paid at controlling and determining the system temperature accurately. Polydimethylsiloxane with an average molecular weight of 150 000 was coated into chromosorb P, AW – DMCS from a solution in n – hexane or toluene. Table 1 shows the experimental specific retention volumes at the studied temperature range. The gas flow rate ranged from 18 to 120 cm³ per minute and the flow rate was found to have no effect on the specific retention volumes.

TABLE I
SPECIFIC RETENTION VOLUMES FOR POLYDIMETHLSILOXANE - HYROCARBON SYSTEMS [3]

Solute	Temperature (°C)		
	25	40	55
n-pentane	80.66	47.6	29.8
n-hexane	227.7	124.2	70.5
benzene	575.1	199.7	112.5
toluene	1032	516.6	269.2

Edison Muzenda is with the Department of Chemical Engineering, University of Johannesburg, Doornfontein, Johannesburg, South Africa, 2028 (tel: 0027115596817; fax: 002711596430; email: emuzenda@uj.ac.za)

Reference [4] obtained specific retention volumes for polydimethylsiloxane – hydrocarbon systems from gas – liquid chromatography. PDMS with an average molecular weight 500 000 was studied. The polymer was coated into chromosorb W support (60-80 mesh acid washed, DMCS treated) from solutions in n-hexane. The coated support was re-sieved and packed into 1,219m, 0.635cm o.d copper tubing which had been previously washed in methanol. Reference [4] used a dual column G.L.C apparatus consisting of Perkin Elmer hot wire thermal conductivity detector. Temperature control was achieved by means of a water bath and was regulated to $\pm 0.05^{\circ}\text{C}$. Experimental temperature was varied from 25 to 70°C , in this range, the solvent (polymer) vapour is negligible. Helium was used as the carrier gas, thus minimising solution effects in the solvent [5]. Reference [4] measured flow rates in the range of 70 to 120 ml/min at room temperature at the detector outlet using soap bubble flow meter. The range was chosen to indicate any flow rate dependence of the elution peaks thus leading to convenient column operation. Inlet pressures were generally in the range 900 -1200mm, while the outlet pressure was always atmospheric. Uniformly symmetrical elution peaks were obtained and considered to confirm the infinite dilution approximation [6] thus representing solute - solvent interactions. The absence of asymmetry in their work resolved difficulties in choosing a suitable working value for the retention time. Reference [4] followed the recommendations of [7] in defining the retention volume by the elution peak maximum. The specific retention volumes are reported in Table 2.

TABLE II:
SPECIFIC RETENTION VOLUMES FOR PDMS - HYDROCARBON SYSTEMS [4]

Solute	Temperature $^{\circ}\text{C}$			
	25	40	55	70
n-pentane	74.76	43.65	27.43	18.33
n-hexane	211.1	114.8	66.45	41.05
n-heptane	587.6	290.8	157.8	89.54
n-octane	1626.6	740.9	367.1	194.9
2-methylpentane	149.9	83.9	51.63	32.21
2-methylhexane	420.9	211.4	119.6	70.04
2-methylheptane	1138	534.7	275.8	150.1
2,2, 4-trimethylpentane	510	260.9	145.8	84.66
benzene	340.4	181.2	105.4	63.43
toluene	959.6	463.7	251.4	141.3
p-xylene	2654.6	1187.5	586.5	307.4
ethylbenzene	2365.7	1090.5	541.2	286.4

Reference [8] studied thermodynamic interactions in polymer systems by gas – liquid chromatography. The dual column GLC apparatus used was similar to that of Summers et al. [4]. All the columns were made of 6.35mm o.d copper tubing, methanol washed prior to use. The supporting solid was chromosorb W (60 -80 mesh, acid washed and DMCS treated). The stationary phase was coated into chromosorb W from a solution of n-hexane. Their findings inform of specific

retention volumes are shown in Table 3.

TABLE III:
SPECIFIC RETENTION VOLUMES FOR PDMS - HYDROCARBON SYSTEMS AT 333K [8]

Probe	Specific retention volumes
n-pentane	24.76
n-hexane	60.91
n-heptane	144.3
n-octane	332.14
n-nonane	765.38
2-methylpentane	46.96
3-methylpentane	52.65
2-methylhexane	107.76
2,4 dimethylpentane	98.97
cyclohexane	106.14
carbon tetrachloride	105.71
benzene	105.46

Reference [9] reported replicate gas – liquid chromatographic technique based specific retention volumes, activity coefficients and interaction parameters of ten volatile organic compounds with PDMS solvent at 303K. The activity and partition coefficient data derived from the GLC method agreed to well within arising experimental errors with the more traditional static apparatus of various designs. Reference [9] used Dow Corning PDMS with an average molecular weight of 89 000. The high precision of GLC apparatus used was essentially identical with those discussed and described by [10]. The polymer was coated into chromosorb G (60 – 80 mesh, acid washed and treated with dimethylchlorosiloxane. The results mainly the specific retention volumes and infinite dilution activity coefficients are presented in Tables 4 and 5.

TABLE IV
VOCs SPECIFIC RETENTION VOLUMES WITH PDMS AT 303K

Solute	Column A	Column B	Column C	% std Dev.
n-pentane	67.05	64.9	66.37	1.66
n-hexane	181.6	177.9	180.2	1.04
n-heptane	484.4	480.1	483.1	0.46
n-octane	1305	1286	1280	1.02
cyclohexane	316.4	213.8	315.2	0.41
methylcyclohexane	575	566.2	567.7	0.83
benzene	291.2	289.7	290.4	0.26
toluene	797.5	785	790.5	0.79
dichloromethane	78.89	78.03	79.23	0.79
chloroform	183	179.8	179.8	0.93

TABLE V

GLC SOLUTE	γ_i^w	γ_i^x	χ_i
	γ_i^w	$10^3(\gamma_i^x)$	χ_i
n-pentane	6.092	4.938	0.36
n-hexane	6.023	5.832	0.402
n-heptane	6.135	6.907	0.458
n-octane	6.342	8.139	0.456
cyclohexane	5.378	5.085	0.262
methylcyclohexane	4.712	4.937	0.752
benzene	6.404	5.62	0.748
toluene	6.457	6.684	0.901
dichloromethane	4.937	4.712	0.64
chloroform	3.366	4.515	-

Ref [6] studied partition coefficients (distribution coefficients) of 14 volatile organic compounds of environmental importance between the gas and liquid phase (PDMS) using two gas chromatographic methods namely isothermal elution and temperature programmed elution. The authors considered some factors which influence the determination of thermodynamic quantities by gas chromatography and suggested some improvements.

III. SUMMARY OF THE AUTHOR'S WORK

The author has studied the interaction of 13 selected volatile organic compounds with polydimethylsiloxane in the form of specific retention volumes and infinite dilution activity coefficients [11] – [14]. The selected VOCs were coded numerically and are shown in Table 6. Four PDMS polymers with average molecular weights 760, 1000, 3200 and 13000 were studied. The interaction studies focused on the effect of temperature, sample size, carrier gas flow rate and column loading [13]. PDMS was coated into Chromosorb P, AW-DMCS or Chromosorb W, AW-DMCS (acid washed, dimethylchlorosiloxane treated) from a solution in chloroform. Ref [14] carried out a detailed study on the influence of temperature on volatile organic compounds-polydimethylsiloxane interactions. Table 7 shows the variation of specific retention volumes of VOCs with PDMS with average molecular weight 3200 studied [14].

TABLE VI
SOLUTE DESCRIPTION AND CODE

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

TABLE VII
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	[9]
2	303	69.9	66.1	5.7	[9]
	313	47.8	47.7	0.3	[9]
3	333	24.9	24.8	0.7	[1]
	303	192.0	179.2	7.1	[9]
	313	126.2	124.2	1.6	[8]
4	333	58.8	60.9	3.5	[1]
	303	508.3	482.5	5.3	[3]
	313	294.6	290.8	1.3	[8]
6	333	146.8	144.3	1.7	[8]
	303	796.5	791.1	0.7	[9]
	313	529.1	516.6	2.4	[3]
7	323	300.2	269.2	11.5	[3]
	303	336.8	315.1	6.9	[3]
8	333	103.4	106.0	2.5	[1]
	303	2645.6	2654.6	0.3	[4]
	313	1223.6	1187.5	3.0	[4]
	333	516.3	536.5	3.8	[3]

The reported specific retention volumes in Table 7 were calculated from corrected peak retention times and column operating conditions using the well-known expression of Littlewood et al. [1]. The retention time used in the calculation of the specific retention volumes was an average of five measurements. Individual retention time values were found to vary by no more than 1% in all cases. The findings of this author [11]-[14] compare very well with literature findings Table 7. Carrier gas was found to have no effect on the specific retention volumes which is in agreement with the work of Pollard and Hardy [15] and Lichtenthaler et al. [3]. This is because the retention time is inversely proportional to the flow rate thus if the mobile phase flow rate is doubled the retention time, t_R will be halved. Absorption was found to be the dominant retention mechanism as the retention volume was directly proportional to the amount of polymer in the column (liquid loading). This was achieved by using columns of different loadings. Therefore quantitative treatment of the data can be performed to calculate various thermodynamic quantities.

ACKNOWLEDGMENT

The Department of Chemical Engineering of the University of Johannesburg is acknowledged for financial support of the studies and conference attendance.

REFERENCES

- [1] B. Littlewood, C. S. G. Phillips, and D. T. Price, "The Chromatography of gases and vapours Part V: Partition analysis with columns of Silicone 702 and Tritolyphosphate," *J. Chem. Soc.*, pp. 1480-1489, 1955.
- [2] D. Patterson, D. D. Deshpande, and H. P. Schreiber "Application of Gas – Liquid Chromatography to the Thermodynamics of polymer solutions," *Macro.*, vol. 4, no. 3, pp. 356-359, 1971.
- [3] R. N. Lichtenthaler, R. D. Newman, and J. M. Prausnitz, "Specific retention volumes from Gas – Liquid Chromatography for Polydimethylsiloxane Hydrocarbon Systems," *Macro.*, vol. 4, no. 4, pp. 650-651, 1973.
- [4] W. R. Summers, Y. B. Tewari, and H. P. Schreiber, "Thermodynamic Interaction in Polydimethylsiloxane – hydrocarbon Systems from Gas – Liquid Chromatography," *Macro.*, vol. 5, no. 1, pp. 11 – 16, 1972.
- [5] D. H. Desty, A. Goldup, G. R. Luckhurst and W. T. Swanton, *Gas Chromatography*, Butterworth, London, 1962, pp. 67
- [6] J. R. Conder, "The derivation of thermodynamic information from asymmetrical chromatographic peaks when more than one distribution mechanism contributes to retention," *J. Chromatogr. A.*, vol. 39, pp. 273-281, 1969.
- [7] A. J. B. Cruickshank, M. L. Windsor, and C. L. Young, "The use of gas-liquid chromatography to determine activity coefficients of mixtures. 1 – Theory and verification of method of analysis," *Proc. R. Soc. Lond. A6* vol. 295, no. 1442, pp. 259-270, December 1969.
- [8] D. D. Deshpande, D. Patterson, H. P. Schreiber, and C. S. Su, "Thermodynamic Interactions in Polymer Systems by Gas – Liquid Chromatography. IV. Interactions between Components in a Mixed Stationary Phase," *Macro*, vol. 7, no. 4, pp. 530-535, 1974.
- [9] A. J. Ashworth, C. F. Chien, D. L. Furio, D. M. Hooker, M. M. Kopečni, R.J. Laub, and G. J. Price, "Comparison of static with gas-chromatographic solute infinite-dilution activity coefficients with polydimethylsiloxane solvent," *Macro.*, vol. 17, no. 5, pp. 1090 – 1094, 1984.
- [10] J. H. Purnell, D. E. Martire, R. J. Laub, "Gas – liquid partition coefficients on n – alkane solutes at infinite dilution in binary n – alkane solvents," *J. Chem. Soc. Faraday Trans.* vol. 2, no. 74, pp. 213 – 221, 1978.
- [11] E. Muzenda, A. Arrowsmith, N. Ashton "Measurement of Infinite Dilution Activity Coefficients for Volatile Organic Compounds in Poly(dimethylsiloxane) by Gas Liquid Chromatography," in *Proc. 61st Annu. Session of the Indian Institute of Chemical Engineers*, Chandigarh, December 2008.
- [12] E. Muzenda, A. Arrowsmith, and N. Ashton, "Study of the Effects of Experimental Variables in Solute Retention Volumes by Gas Liquid Chromatography (glc) in Polymer Solution Thermodynamics," in *Proc. 61st Annu. Session of the Indian Institute of Chemical Engineers*, Chandigarh, December 2008.
- [13] 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.*, vol. 27, no. 5, pp.1509-1512, May 2010.
- [14] E. Muzenda, and F. Ntuli "Temperature effect on volatile organic compounds polydimethylsiloxane interactions," *IJCEA.*, vol. 2, no. 6, pp. 376-380, 2012.
- [15] F. H. Pollard and C.T. Hardy, *Vapour Phase Chromatography*, Butterworth, London, 1957.