Measurement of Infinite Dilution Activity Coefficients of Selected Environmentally Important Volatile Organic Compounds in Polydimethylsiloxane using Gas – Liquid Chromatography

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Abstract - Silicon oil chemically known as polydimethylsiloxane (PDMS) is a high boiling point solvent highly suitable for volatile organic compounds (VOCs) absorption. In order to use PDMS as an absorption solvent for a specific waste gas problem, it is important to determine the infinite dilution activity coefficients of the VOCs to be separated with PDMS. This work reports activity coefficients at infinite dilution of 13 VOCs in polydimethysiloxane determined by the dynamic gas liquid chromatographic technique. The measurements were carried out at various temperatures (i.e, 303.15, 313.15, 323.15., 333.15, 353.15, 373.15, 393.15 and 423.15K). Four PDMS polymers with average molecular weight ranging from 760 to 13 000 were used as solvents. A control column packed by Perkin Elmer to our specifications was used to validate the coating and packing methods. Flow rate dependence of the elution peaks was also investigated by varying it from 10 – 50 ml/min. Precision was improved by reproducing the results using columns with different liquid loading, thus also studying the retention mechanism. The results compare well with the data from previous work using simple headspace and UNIFAC predictions and literature values. 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.

Key Words: Volatile organic compounds; thermodynamics; polydimethysiloxane; activity coefficient, retention mechanism.

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INTRODUCTION

The infinite dilution activity coefficients (γ_i^∞) of solutes are very important for the design of separation processes such as absorption, eg when trace contents have to be removed from contaminated air streams. In this paper we dealt with 13 compounds of environmental significance. The γ_i^∞ of *n*–pentane, *n*–hexane, *n*–heptane, triethylamine, toluene, xylene, cyclohexane, butylacetate, diethylether, chloroform, acetone, ethylmethylketone and isobutylmethylketone were measured by gas – liquid chromatography (GLC) using four polydimethysiloxane (PDMS) polymers as stationary phases. The measurements were carried out at several temperatures between 303.15 and 423.15K under atmospheric pressure. The GLC method is suitable for the measurement of activity coefficients at infinite dilution because of the negligible vapour pressure of PDMS. Using this procedure data can be obtained quickly although careful measurement is necessary for accuracy. In this work the effect of carrier gas flow rate and sample size on retention volumes were studied. From the retention data, solute activity coefficient at infinite dilution and other thermodynamic properties of mixing can be easily obtained. The γ_i^∞ give a direct measure of interactions between unlike molecules in the absence of solute – solute interactions.

High polymers lie somewhat between conventional crystalline solids and ordinary liquids with respect to viscosity and diffusivity of small molecules in the polymer, hence two mechanisms of solute sorption may exist. Absorption of solutes in the bulk polymer phase or adsorption of solutes in the polymer surfaces maybe responsible for sorption. A quantitative treatment of the data is best carried out when absorption is the dominant mechanism. When the solute is held back by absorption only, the retention volume is directly proportional to the amount of liquid loading in the column. Adsorption, on the other hand, may influence chromatographic retention values as reported and reviewed by Heberger et al. (2002). For example, the influence is enhanced if the solute does not dissolve in the stationary liquid phase, then proportionality between retention volume and surface area is observed.

In order to use PDMS as absorption solvent for a specific waste gas problem, it is important to determine the infinite dilution activity coefficients of the VOCs to be separated with PDMS. Therefore, this work reports activity coefficients at infinite dilution of 13 VOCs in polydimethylsiloxane determined by the dynamic gas liquid chromatographic technique.

EXPERIMENTAL

The apparatus used has been described previously (Muzenda et al., 2000, 2002, 2008). The carrier gas was helium minimizing solution effects in the solvent as reported by Desty et al., (1962). 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. Flow rates in the range of 20 to 50 ml/min were measured by a soap bulb flow meter at the detector outlet. Inlet pressure was controlled by precision regulators and measured by an inlet pressure gauge. Inlet pressure ranged from 900 - 1100mm Hg while outlet pressure was always atmospheric. 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). A variation of sample size was found by measuring the peak positions (retention volumes) for small sized samples.

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. Materials

Four PDMS polymers from Dow Corning were used as described in Table 1. With the exception of column 4 packed by Perkin Elmer, in the other three columns PDMS were coated into Chromosorb P support (60 – 80 mesh). Thirteen solutes with purity above 99% coded numerically as in Table 2 for simplicity were used in this work.

Table 2: Solute Description and Code

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

CALCULATIONS

A mixture of *n*–pentane, *n*–hexane and *n*–heptane was injected into the column and the gas holdup time was calculated from equation (1)

$$t_M = \frac{t_{R_1} t_{R_3} - t_{R_2}^2}{t_{R_1} + t_{R_3} - 2t_{R_2}} \tag{1}$$

The net retention volume(V_N) is obtained from equation (2)

$$V_N = j_3^2 F_o \left(t_R - t_M\right) \tag{2}$$

The factor j_3^2 in equation (2) corrects for the influence of pressure drop along the column and its given by equation (3) (Grant, 1971).

$$j_3^2 = \frac{3}{2}\frac{\left[\left(\frac{P_i}{P_o}\right)^2 - 1\right]}{\left[\left(\frac{P_i}{P_o}\right)^3 - 1\right]} \tag{3}$$

Where P_i and P_o are, respectively, the inlet and outlet pressures of the gas chromatography column. The specific retention volume (V_g^0) was calculated from the following expression

$$V_g^0 = \frac{273.15 V_N}{W_s T_c} \tag{4}$$

Mole – and weight fraction based activity coefficients at infinite dilution of solute 1 in stationary phase 2 were calculated using equations (5) and (6) respectively

$$\ln {}^x\gamma_1^\infty = \ln \frac{273.16}{V_g^0 P_1^o M_s} - \frac{P_1^o\left(B_{11} - \bar{V}_1^o\right)}{RT} \tag{5}$$

$${}^w\gamma_1^\infty = \left({}^x\gamma_1^\infty\right) M_s / M_1 \tag{6}$$

In equations (5) and (6) R is the ideal gas constant, T is the temperature of column, B_{11} is the second virial coefficient of the solute in the gaseous state at temperature T, P_1^o is the vapour pressure of the pure solute at temperature T and M_2 is the average polymer molecular weight, The values P_1^o and B_{11} were taken from literature (Timmermans, 1950 and 1965) either at the same conditions or extrapolated to the conditions under study.

RESULTS AND DISCUSSION

1. Infinite dilution activity coefficients

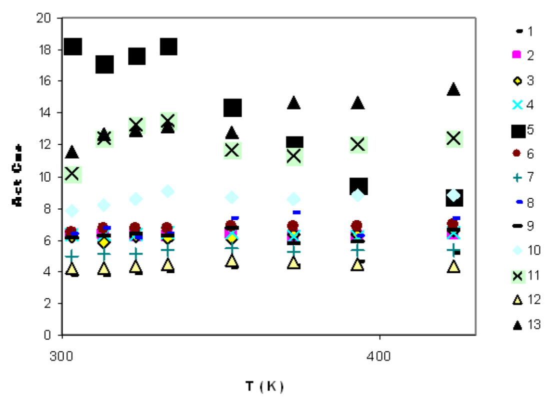

Fig 1. Influence of temperature (Column1)

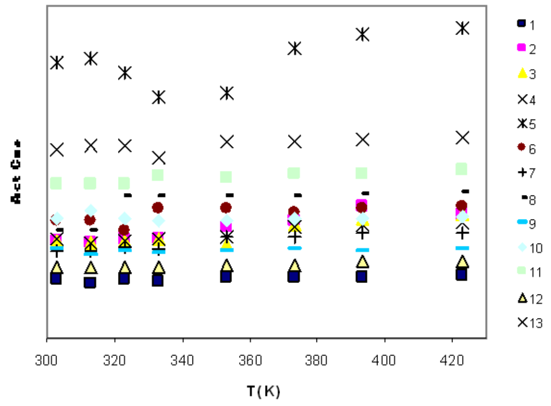

Fig 2. Influence of temperature (Column2)

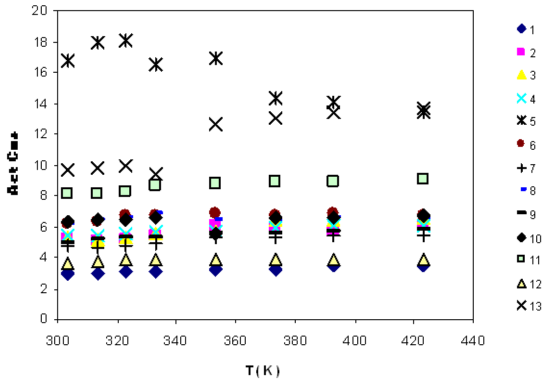

Fig 3. Influence of temperature (Column 3)

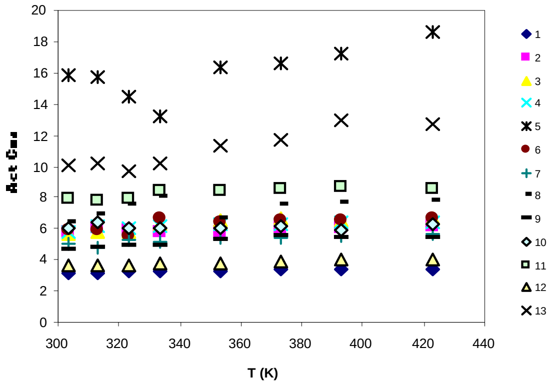

Fig 4. Influence of temperature (Column 4)

Activity coefficients at infinite dilution of 13 volatile organic compounds in the four columns measured at 303.15, 313,15, 323.15, 333.15, 353.15, 373.15, 393.15 and 423.15K are shown in figures 1 to 4. The mole and weight fraction based γ_i^∞ were calculated using equations (5) and (6). Each value is an average of 5 repetitive runs and individual runs were found to vary by no more than 1%. The runs were carried out in such an order that no systematic error in the control of chromatographic conditions could influence the results collected for any single column or compound. The γ_i^∞ for *n*–pentane, *n*–hexane, *n*–heptane, cyclohexane, toluene and chloroform measured at 303.15K in this work are in agreement with those of Summers at al. (1972) and Ashworth et al. (1984). The close agreement means that our results for the rest of the compounds studied here are considered to be accurate and reliable. The variation of γ_i^∞ with temperature presented in figures 1 to 4 show similar behaviour to that obtained by Inoue et al. (2007) .

2. Effect of liquid loading

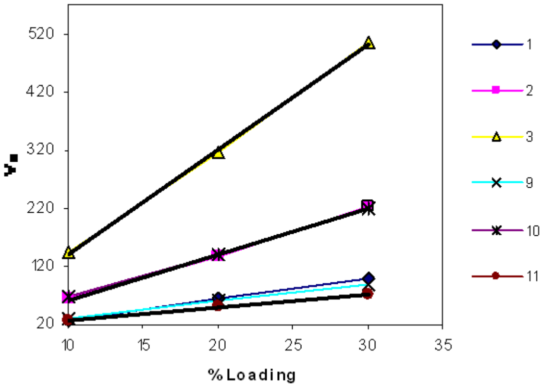

Fig 5a. Effect of liquid loading on Vg

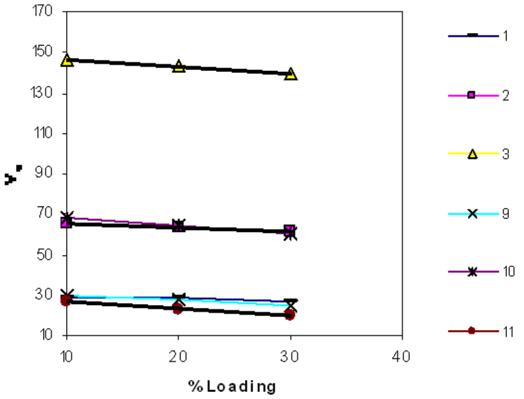

Fig 5b. Effect of liquid loading on Vn

Different columns were prepared containing various amounts of PDMS to investigate sorption mechanisms. Figures 5a and 5b show that a direct proportionality exists between retention volumes and liquid loading, thus solutes are held back exclusively by absorption. Therefore experimental results were not affected by solute adsorption on polymer surface and solid support.

3. Effect of carrier gas flow rate

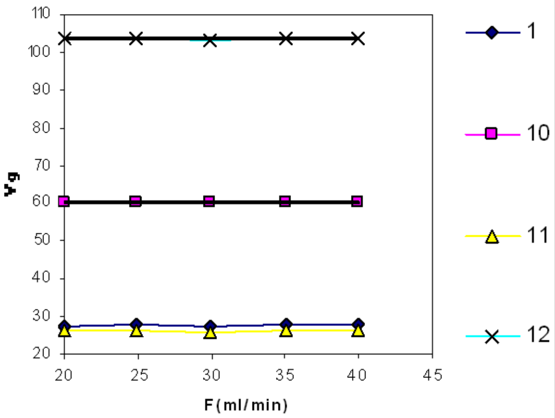

Fig 6a. Effect of carrier gas flowrate on Vg

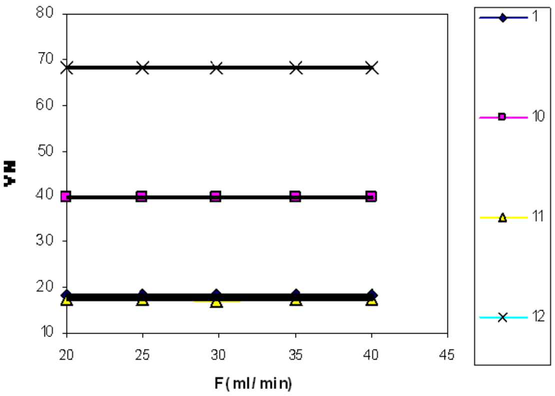

Fig 6b. Effect of carrier gas flowrate on Vn

In this work carrier gas flow rate was varied from 20 to 40ml/min and no significant change was observed on both the net and specific retention volumes. This means that carrier gas flow rate has no effect on the infinite dilution activity coefficients. This is in agreement with work reported by Pollard et al. (1957) and Lichtenthaler et al. (1973). 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. However Inoue et al. (2007) found that infinite dilution activity coefficients of n – alkanes in 4 – methyl – n- butylpyridinium tetrafluoroborate were affected by the flow rate of the carrier gas.

4. Effect of sample size

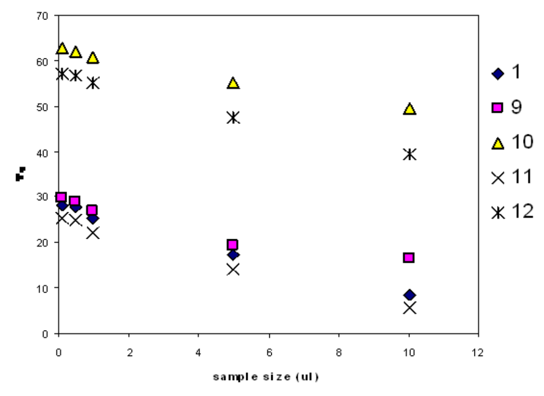

Fig 7a. Effect of sample size on Vg

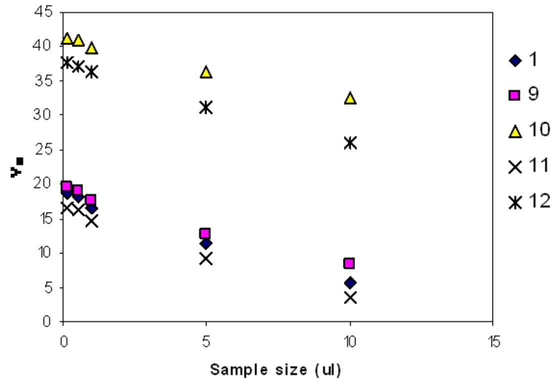

Fig 7b. Effect of sample size on Vn

The V_N and V_g of pentane, diethylether, chloroform, acetone and ethylmethlketone were measured at varying sample sizes of 0.1 to 10µl at constant flow rate of 40.01ml/min and temperature of 333.1K in column 4. As shown in figures 7a and 7b, the retention times were affected by the volume of samples. This tendency is in accordance to the polymer solute systems reported by Inoue et al. (2007) and that for sample sizes less than 0.1µl, retention times were independent of sample volumes.

CONCLUSIONS

The infinite dilution activity coefficients of n–pentane, n–hexane, n–heptane, triethylamine, toluene, xylene, cyclohexane, butylacetate, diethylether, chloroform, acetone, ethylmethylketone and isobutylmethylketone were measured by GLC at 303.15 – 423.15K under atmospheric conditions. Infinite dilution activity coefficients were affected by the sample size of the solutes and were determined to satisfy the infinite dilution condition. Absorption was confirmed to be the main sorption mechanism. The results are in good agreement with those obtained from previous work using static headspace methods and literature values. Complete coverage of supporting surfaces by the stationary phase is necessary if elution data is to be free from the influence of adsorption effects. We can conclude that PDMS can be used to effectively absorb volatile organic compounds from contaminated waste air / gaseous streams.

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