CHARACTERISTICS OF RETENTION IN GAS–LIQUID CHROMATOGRAPHY

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SUMMARY

Specific retention volumes and heats of solution were measured in squalane and oxydipropionitrile by using static and chromatographic techniques. It was shown that the specific retention volumes obtained by using the two techniques had the same values for non-polar systems. The chromatographic solutions had smaller entropies than the classical ones. It was found that the chromatographic solutions had more rigid structures than classical ones. The entropy part of the retention increased with a decrease in the amount of stationary phase on a support. Experimental conditions for the accurate measurement of retention volumes for identification purposes were determined. The heat of solution is almost independent of the amount of stationary phase on a support.

INTRODUCTION

It has been shown by many workers (for example, refs. 1 and 2) that distribution coefficients as measured by static and gas chromatographic methods are equal. Chromatography enables the characteristics of very dilute solutions to be estimated. The static technique does not have a high accuracy at these low concentrations. It is possible that the sensitivity and the precision of the static technique are increased when the chromatographic method of analysis is used[3,4] and this is the reason for comparing the characteristics of solutions by static and chromatographic techniques under the same conditions.

The main aim of this paper is the comparison of characteristics of retention obtained by using chromatographic and static techniques for different systems. This comparison was carried out for different amounts of a stationary phase in the chromatographic column.

EXPERIMENTAL

We chose as solvents two standard stationary phases: squalane (non-polar) and oxydipropionitrile (strongly polar). We chose as solutes the following substances: benzene, cyclohexane, *n*-hexane, acetone, methyl ethyl ketone and chloroform.

Chromatographic measurements of solubility were carried out by using a Varian-1860 chromatograph with a catharometer and hydrogen as the carrier gas. The chromatographic column (diameter 2.5 mm, length 1.5 m) was filled with Chromosorb W, impregnated with the stationary phase. The solid support was silanized when squalane was used as the stationary phase. Specific retention volumes (V_g) and heats of solution were calculated as in ref. 5. The oven temperature was held constant to within *ca.* 0.1°. The amount of stationary phase in the column was measured by weighing the sorbent. The chromatographic columns were maintained at a temperature of 90° for 4 h before experiments. The standard deviation of the specific retention volume was 1% and that of the heat of solution was 0.15 kcal/mole.

The determination of the solubility in classical systems was carried out in a glass saturator (volume 60 ml)[4]. A 10-g amount of a solvent and a measured amount of a solute were placed in the saturator, which was maintained at a constant temperature. The equilibrium concentration of the solute in the gas phase was measured by using a Chrom-31 chromatograph with a flame ionization detector and integrator after the establishment of equilibrium in the saturator (about 1 h). The 0.8-m chromatographic column was filled with Chromosorb W coated with squalane. The temperature of the resolution was 70°. A sample of gas was taken from the saturator with a thermostated Hamilton syringe (0.1-ml). The distribution of the solute between the two phases was calculated from the analytical chromatographic data and from the weighing data. The static distribution coefficient was expressed by using the specific retention volume for comparing chromatographic and static data in the same units. The accuracy of the static method depends on the accuracy of the chromatographic determination of the concentration of the solute in the gas phase. The absolute calibration of the chromatograph was carried out by using vapours of the pure solutes at constant temperature. The standard deviation of the static retention volume was 2% and that of the static heat of solution was 0.2 kcal/mole. The lower limit of the concentrations of the classical solutions under study was 0.1%.

The standard temperature for the comparison was 50°.

RESULTS

Fig. 1 shows the relationships between the chromatographic specific retention volumes and the amount of the stationary phases on the solid support. It has been shown[6,7] that retention in gas–liquid chromatography (GLC) depends on the interphase adsorption. Retention volumes of the solutes were measured on the pure silanized solid support to determine the adsorption on the solid.

The result obtained for benzene on silanized Chromosorb W was 3.4 ml. This value is the maximum possible adsorption of benzene on a solid support. The adsorption of substances decreases when the solid support is coated with a stationary phase. The adsorption on an actual GLC column is measured by extrapolating the relationship between the retention volume of benzene and the amount of stationary phase on 10 ml of support (M) to the level at which $M = 0$. The values obtained for the adsorption of benzene on the squalane column was 3.0 ml and on the oxydipropionitrile column 2.2 ml. Curves 2 and 4 in Fig. 1 are corrected for the adsorption value relations. These curves show the influence of M on the solubility of benzene. They have a small minimum and then the solubility increases to a constant value.
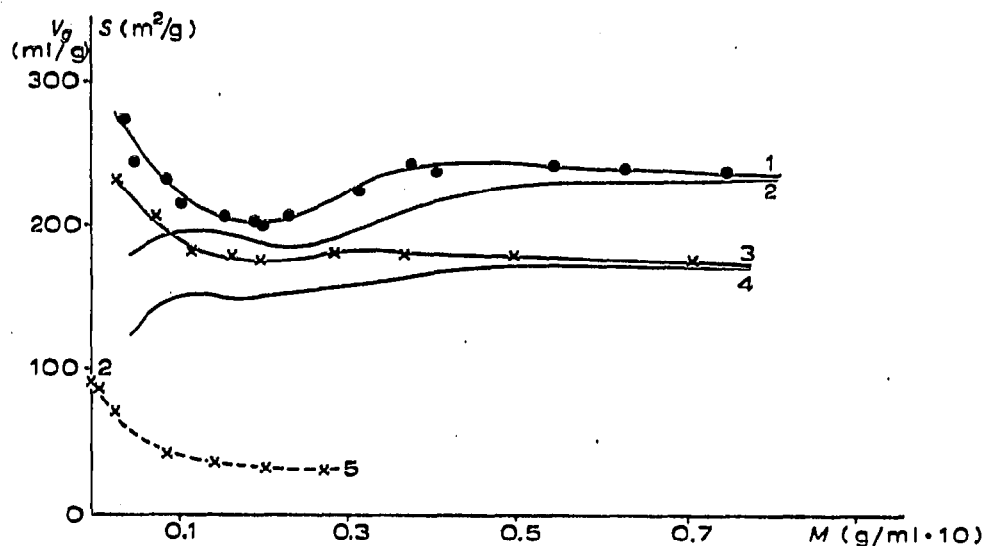
Fig. 1. Relationship between V_g (ml/g) and M (g of stationary phase on 10 ml of support). Solute: benzene. Curves 1 and 2 refer to squalane, 3 and 4 to oxydipropionitrile.

The specific retention volume increases at low values of M (about 0.1% of squalane) because the surface of the liquid is increased by the increasing amount of the liquid layer on the solid support[8]. Then, after coating the solid support, the liquid surface decreases with increasing amounts of the liquid (curve 5) to an almost constant value. However, curve 2 increases to a constant value. Heats of solution of benzene are constant within the limits under study, and therefore all deviations are related to the entropy of solution. We calculated the entropy from the equation:

$$K = \frac{K_1}{N_1 RT}$$

K is the thermodynamic partition coefficient, calculated from the "chromatographic" partition coefficient K_1 (refs. 9 and 9a); N_1 is the number of moles of stationary phase per unit volume; ΔS_s is the standard entropy of solution; and ΔH_s is the standard enthalpy of solution, calculated from the temperature relationship of V_g (ref. 5).

The chosen standard states are a 1-atm. ideal gas standard state and an infinitely dilute solution for the liquid-phase solute.

The calculated value for the standard entropy with $M = 0.2$ is less by 0.4 e.u. than the standard entropy of solution with $M = 0.5$. The values of V_g for benzene in squalane measured by static and chromatographic methods are the same, but the value of $\Delta H_{s,\text{static}}$ is less by 0.2 kcal/mole than the value of $\Delta H_{s,\text{chromatographic}}$. Then the value of the standard entropy of a static solution is higher by 0.6 e.u. than that for a chromatographic solution. A similar relationship is obtained for chromatographic solutions of benzene in oxydipropionitrile.

DISCUSSION

The relationships obtained can now be discussed. A stationary phase on the surface of a solid support exists in two different states: an adsorbed liquid and a

capillary liquid[10]. Features of these different states are also different, and therefore solubilities in these liquid types must be different. The liquid in the capillaries of the solid support has the same features as the pure liquid[10]. A strong adsorption potential causes a regular arrangement of the molecules in the adsorbed layer. Entropy decreases when a system assumes a more regular structure. Therefore, the entropy of solution in the adsorbed layer of the liquid is smaller than that for the pure liquid. This is the reason for the small values of V_g at low values of M when the adsorbed liquid is the main component of the liquid in the GLC column. When the amount of the stationary phase on the support is increased, the proportion of the adsorbed liquid in the GLC column is decreased. Then the solubility in the GLC column approaches the solubility in the pure liquid.

The experimental data obtained therefore show the complexity of the solubility process in GLC columns. The heat of solution has an almost constant value when the value of M is changed. The entropy of solution is the main factor which influences the GLC solubility when the value of M is changed.

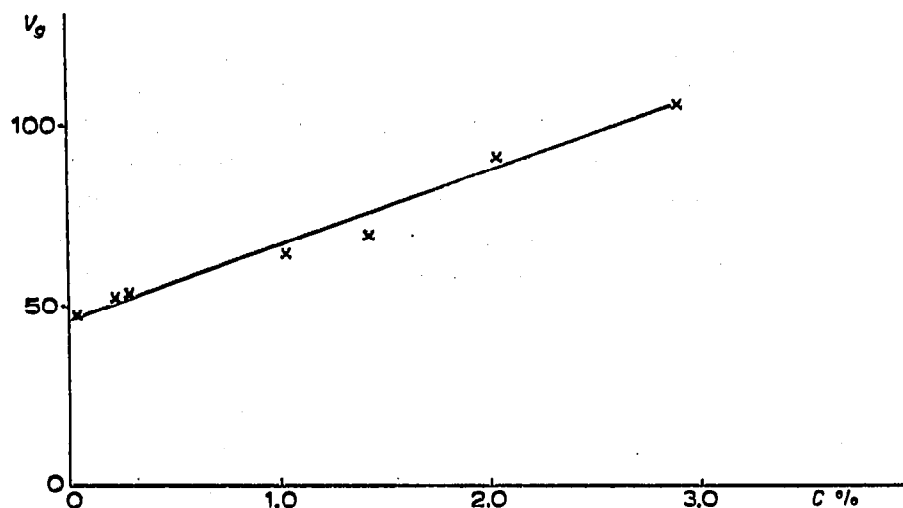The static measurements of V_g in non-polar systems show that the concen-

Fig. 2. Relationship between static V_g for benzene and the concentration (C) of the solution. Solvent: oxydipropionitrile.

tration of a solution has no influence on V_g. We obtained a different relationship for solutions of benzene in oxydipropionitrile (Fig. 2): the static specific retention volume increased rapidly as the concentration of the solution increased. The static heat of solution is constant within the limits under study, which indicates the change of the structure of the solution by increasing the concentration of benzene in oxydipropionitrile.

The relationships between the specific retention volumes of some substances in squalane are given in Fig. 3. The results were similar to those for benzene. An influence of the stationary phase surface on V_g can be seen at small values of M, when V_g decreases as the amount of the stationary phase increases (to $M = 0.2$). The experimental data show that adsorption on the liquid surface has a great influence on the value of V_g for hydrocarbons: the large surface of the hydrocarbon molecule
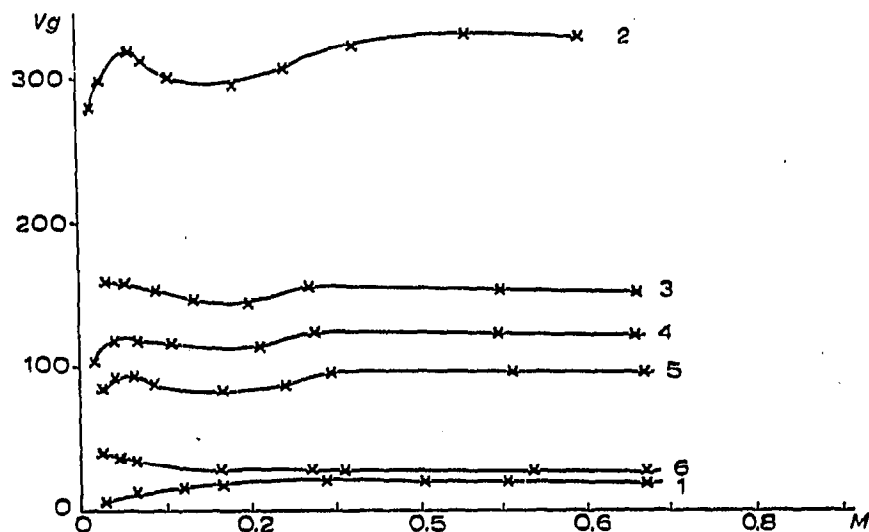
Fig. 3. Relationship between V_g and M. Solvent: (1) oxydipropionitrile; (2–6) squalane. 1 and 2, cyclohexane; 3, hexane; 4, chloroform; 5, methyl ethyl ketone; 6, acetone. All V_g are corrected for the value of the adsorption on the support.

increases the adsorption. Thus, for example, the surfaces of the chloroform and hexane molecules are very different, but the retention volumes of these substances are similar; the adsorption part of the retention of hexane is greater than that for chloroform. The comparison of the gas chromatographic and static values of the thermodynamic functions of solution for polar molecules in non-polar solvents has been carried out in previous works[11,12].
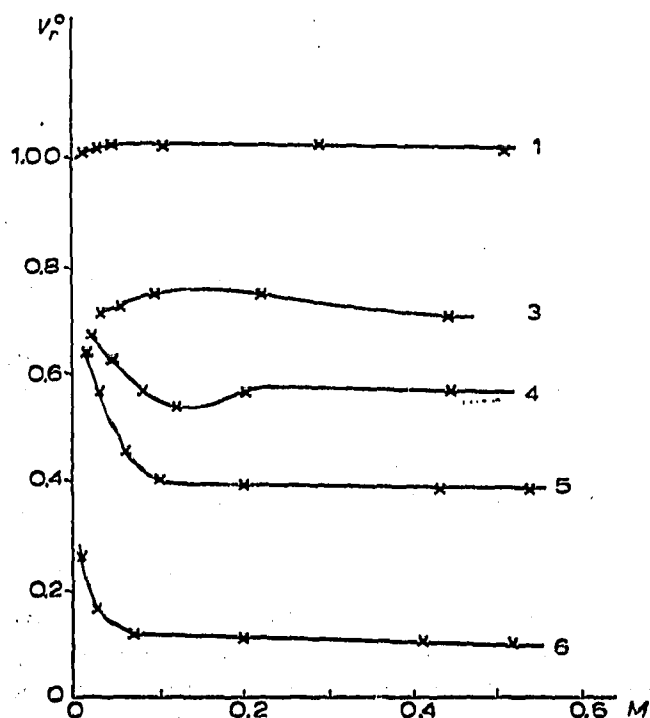

Fig. 4. Relationship between relative retention volumes and M for squalane. Curves as in Fig. 3.

V_r^o

1.5 —

1.0 —

0.5 —

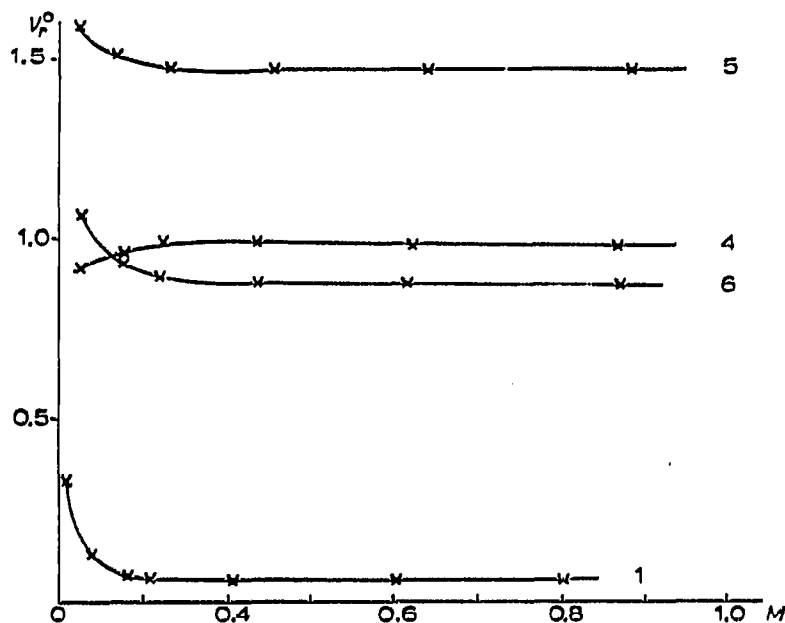0   0.4   0.6   0.8   1.0 M

Fig. 5. Relationship between relative retention volumes and M for oxydipropionitrile. Curves as in Fig. 3.

The relationships between relative retention volumes V_r^o on squalane and the values of M are given in Fig. 4. These experimental data show that the values of relative retention are stabilized more rapidly than the values of V_g, which is connected with some compensation effects. The relative retention volumes are stabilized when $M \geqslant 0.2$. The relative heats of solution are almost constant at all values of M.

The relationships between relative retention volumes on oxydipropionitrile and M are given in Fig. 5. These data show that the relative retention volumes are stabilized after $M = 0.1$. An example of the change of the specific volume of cyclohexane on oxydipropionitrile is given in Fig. 3. This relationship is the same as that for benzene.

Consequently, the experimental data obtained enable the thermodynamic functions of solution in chromatographic and classical systems to be compared at low concentrations. Specific retention volumes for non-polar systems are the same for chromatographic solutions as those for classical solutions (M must be greater than 0.3). However, the thermodynamic functions of solution for the systems under comparison are different: chromatographic solutions have greater heats of solution than classical solutions. The solvent on the support surface has a more regular structure than the pure liquid. The heats of solution of non-polar solutes in polar chromatographic solvents are also greater than those for classical systems (about 0.5 kcal/mole for benzene). Consequently, the chromatographic solutions have more rigid structures than classical solutions.

Heats of solution in chromatographic systems do not depend on M for $M = 0.1-0.8$, but the chromatographic entropy of solution increases with increasing M up to $M = 0.4$. The value of M must be greater than 0.3 to obtain real values of V_g, and must be greater than 0.2 for measurement of relative retention volumes to be carried out. These recommended amounts of stationary phases must be used to eliminate possible errors during identifications on the basis of retention volumes.

Also, the possibility of changing the selectivity of a stationary phase occurs with changes in the value of M. Small amounts of a stationary phase can be used for a resolution when the components of a mixture have different entropies of solution. The entropy factor of the selectivity has greater importance for small values of M.

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