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## INTERACTIONS OF POLAR SOLUTES WITH NON-POLAR STATIONARY PHASES IN GAS-LIQUID CHROMATOGRAPHY

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## SUMMARY

The gas chromatographic solutions of polar substances in a non-polar stationary phase were studied. The semiempirical method of calculation of dispersion forces in such solutions is discussed. A comparison of gas chromatographic and static values of heats of solution shows that the concentration effect has great importance in the systems under study. The values of concentration effects were tabulated for the different chemical classes of substances.

The calculation of the thermodynamic functions of solution is the main problem in the theory of the selectivity of stationary phases in gas-liquid chromatography (GLC)<sup>1</sup>. The development of semiempirical methods of calculation of these values provides an opportunity for identifications to be made in gas chromatography. The heat of solution is one of two independent thermodynamic functions of solution which are used to describe the selectivity of stationary phases. Unlike the logarithm of the retention volume, the heat of solution can be calculated on the basis of additivity principles with sufficient accuracy. Microcharacteristics of atomic groups of solute molecules are used for such calculations<sup>2</sup>. The intermolecular forces in non-polar stationary phases consist of dispersion and induction forces. Therefore we have the simplest case for calculations using non-polar stationary phases.

In the case of non-polar substances as solutes and solvents, the heat of solution can be calculated as follows:

$$\Delta H_s = \Delta H_d - \Delta H_h \quad (1)$$

where

$\Delta H_s$  is the heat of solution;

$\Delta H_d$  is the heat of solution which represents the energy of the dispersion interaction;

$\Delta H_h$  is the heat of hole formation.

The last term of this equation is measured experimentally<sup>2</sup>.

$$\Delta H_d = 0.3 m \quad (2)$$

where  $m$  is the amount of branching of the main chain of the solute molecule (the

heat of hole formation is negligibly small for linear chain molecules in paraffin solvents).

$$D_i = \frac{\alpha_1 \alpha_2}{r^6},$$

$$i = \frac{\Delta H_{sp}}{\sum_p K_i D_i},$$

$$\Delta H_d = i \sum D_i K_i \quad (3)$$

where

$\alpha_1$  is the polarisability of the atomic group of the solute;

$\alpha_2$  is the polarisability of the methylene group (non-polar solvent);

$r$  is the sum of the van der Waals radii of the atomic group of the solute and of the solvent (for the solvent  $r = 2\text{\AA}$  as for the methylene group);

$\Delta H_{sp}$  and  $\sum_p K_i D_i$  refer to  $n$ -paraffins which have the same number of carbon atoms as the sum of heavy atoms of the solute (for example, the value of  $i$  for  $n$ -butane is used for the calculations of heats of solution of  $n$ -propyl chloride);

$K_i$  is the coefficient of the intramolecular shielding of the atoms and of the atomic groups in the solute molecule<sup>2</sup>.

The calculation of heats of solution should give sufficient exact data concerning non-polar isomeric substances; the resolution and identification of isomeric substances being one of the most difficult problems in gas chromatography. The investigation of the usefulness of this method of calculation for the solutions of polar substances in non-polar phases is reported in this paper.

The induction forces are induced on dissolving polar substances in non-polar solvents. A concentration effect<sup>3</sup> also occurs in such systems. The last effect is connected with the association of polar molecules in a non-polar environment. The heat of solution of aggregates of polar molecules is greater than the heat of solution of an individual molecule. Therefore, the induction forces and concentration effect lead to an increase in the heat of solution of polar substances in non-polar solvents as compared with the values calculated by eqns. 1-3.

Squalane is used for the experimental investigation of the solubility of polar substances. The chromatographic measurements of the heats of solution were made using "Varian-1860" and "Chrom-31" chromatographs. The temperature of the chromatographic column varied from 30 to 80°. The length of the column is 1.5 m. Squalane (0.25 g) is added to 10 ml silanised Chromosorb W. The standard deviation of the retention volumes is 0.4%; the standard deviation of the heats of solution is 0.1 kcal. A commonly used equation<sup>4</sup> is used for the calculation of the heats of solution from temperature relationships of specific retention volume.

The experimental and the calculated values, on the basis of eqns. 1-3, are listed in Table I. The calculated data show the value of the dispersion interactions. The difference between experimental and calculated heats of solution together with  $\Delta H_h$  describes the sum of induction forces and the concentration effect ( $\Delta$ ). A comparison of  $\Delta$  values shows that these values decrease in an homologous series. A constant value of  $\Delta$  is established after the fourth to fifth members of a series.

Let us consider the possible reasons for the appearance of the  $\Delta$  value in

TABLE I

COMPARISON OF CALCULATED ( $\Delta H_d$ ) AND EXPERIMENTAL ( $\Delta H_s$ ) HEATS OF SOLUTION OF DIFFERENT CHEMICAL CLASSES OF SUBSTANCES (kcal/mole)

| Substance                    | $\Sigma K_i D_i$ | $\Delta H_d$ | $\Delta H_h$ | $\Delta H_s$ | $\Delta$ |
|------------------------------|------------------|--------------|--------------|--------------|----------|
| Allyl alcohol                | 13.4             | 4.0          | —            | 7.25         | 3.25     |
| <i>n</i> -Propanol           | 13.4             | 4.0          | —            | 7.2          | 3.2      |
| Isopropanol                  | 13.3             | 4.0          | 0.3          | 6.65         | 2.9      |
| <i>tert.</i> -Butanol        | 15.3             | 4.9          | 0.6          | 6.8          | 2.5      |
| Nitromethane                 | 17.4             | 5.25         | 0.2          | 8.0          | 1.95     |
| Ethyl chloride               | 14.0             | 4.07         | —            | 5.3          | 1.2      |
| 1-Chloropentane              | 21.6             | 7.35         | —            | 8.5          | 1.1      |
| 1,2-Dichloroethane           | 18.2             | 5.45         | —            | 6.3          | 0.85     |
| 1,1-Dichloroethane           | 18.2             | 5.45         | 0.3          | 6.05         | 0.9      |
| 1,1,2-Trichloroethane        | 22.5             | 7.22         | 0.3          | 7.7          | 0.8      |
| Isobutyl chloride            | 18.9             | 6.05         | 0.3          | 6.55         | 0.8      |
| <i>sec.</i> -Butyl chloride  | 19.0             | 6.08         | 0.3          | 6.45         | 0.7      |
| <i>tert.</i> -Butyl chloride | 18.5             | 5.95         | 0.6          | 5.25         | —0.1     |
| Carbon tetrachloride         | 23.2             | 7.4          | 0.6          | 7.0          | 0.2      |
| Ethyl bromide                | 15.5             | 4.50         | —            | 5.50         | 1.0      |
| <i>sec.</i> -Butyl bromide   | 19.7             | 6.32         | 0.3          | 6.8          | 0.8      |
| Acetone                      | 14.4             | 4.35         | 0.2          | 5.05         | 0.9      |
| Methyl ethyl ketone          | 17.0             | 5.45         | 0.2          | 6.1          | 0.85     |
| Butyral                      | 16.1             | 5.15         | —            | 5.8          | 0.65     |
| Acetonitrile                 | 14.9             | 4.45         | —            | 4.55         | 0.1      |
| Ethyl acetate                | 20.4             | 6.55         | 0.2          | 6.25         | —0.1     |
| <i>n</i> -Propyl acetate     | 23.0             | 7.85         | 0.2          | 7.6          | —0.05    |

squalane. The value of the induction forces is increased with the dipole moments of molecules. If the induction forces are the main tail of  $\Delta$ , we will expect that nitriles and ketones have the greatest values of  $\Delta$ . As a matter of fact the experimental data show that alcohols have the greatest values of  $\Delta$ . Alcohols have a high ability to associate. Consequently, we can suppose that the discrepancies between the experimental and calculated heats of solution in squalane mainly refer to a concentration effect.

Some experiments on the measurement of the solubility have been carried out for a more detailed investigation of the nature of  $\Delta$ . The solubility is measured as relation between the concentrations of the solute in liquid and gaseous phases, using chromatography for analysis of the gas phase<sup>1</sup>. Squalane (10 g) is placed in a glass saturator (60 ml) which is closed by a plastic cork. The cork has a hole. A gas sample is taken from the saturator through the hole in the cork. The Hamilton teflon syringe with fixed volume is used for sampling (volume is 0.025 ml). A measured sample of solute is placed in the saturator then the saturator is maintained at a constant temperature for 20–40 min. The gas sample is then taken to "Chrom-31" gas chromatograph which is fitted with a flame ionisation detector and integrator. This chromatograph has a column coated with squalane and a temperature of 70°. Specific retention volumes are calculated from static measurements for comparison with the chromatographic data. The heats of solution in the static measurements are calculated from the temperature dependence of specific retention volumes. The average error of the measurements of the heats of solution by the static method is *ca.* 0.2 kcal. The measurements are made within a temperature interval 20–60° and a concentration interval of 0.05–1.5%.

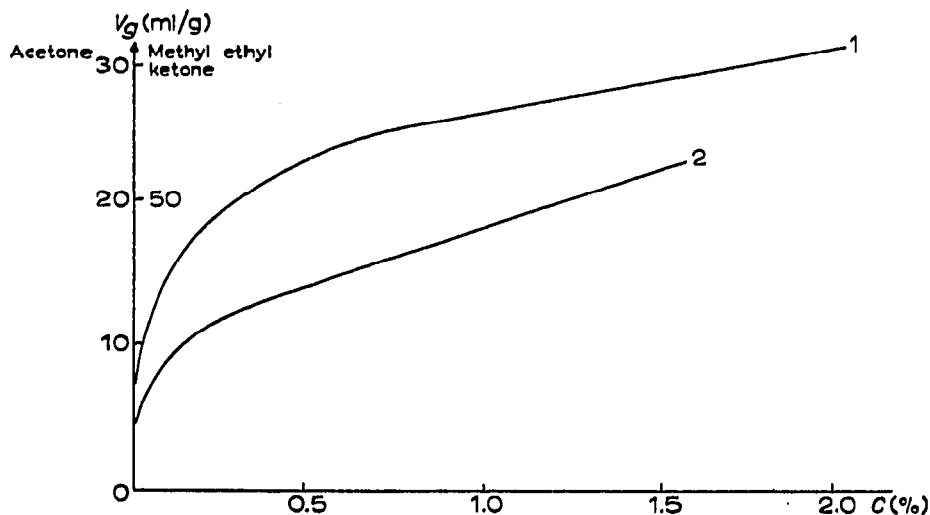


Fig. 1. Relationship between  $V_g$  of acetone (2), methyl ethyl ketone (1) and concentration of solution in squalane (%).

The concentration relationship of the specific retention volume is shown in Fig. 1. These data were obtained for acetone and methyl ethyl ketone at 50°. It is clear that the solubility of polar solutes in a non-polar solvent increases with concentration. This increase is greater for low concentrations and for acetone. The latter fact explains the effect of a decreasing  $\Delta$  value in an homologous series. The values of the heats of solution of acetone and methyl ethyl ketone in squalane are listed in Table II. The heat of solution is a logarithmic function of the specific retention volume, therefore the increase of the heats of solution with concentration is smaller than for specific retention volume.

The comparison of chromatographic and static heats of solution shows that the average effective concentration of gas chromatographic solutions is *ca.* 0.1%. The retention data of benzene and hexane are independent of concentration.

Consequently the retention data and the results of the static measurements show that the  $\Delta$  value depends mainly on the concentration effect.

The comparison of the data in Table I allows one to write the following series

TABLE II

COMPARISON OF CHROMATOGRAPHIC AND STATIC HEATS OF SOLUTION OF ACETONE AND OF METHYL ETHYL KETONE IN SQUALANE (kcal/mole)

| Substance           | Method | $\Delta H_s$ | Concentration (%) |
|---------------------|--------|--------------|-------------------|
| Acetone             | Chrom. | 5.05         |                   |
|                     | Static | 4.6          | 0.007             |
|                     |        | 5.4          | 0.2               |
| Methyl ethyl ketone | Chrom. | 6.1          |                   |
|                     | Static | 5.8          | 0.01              |
|                     |        | 6.2          | 0.03              |
|                     |        | 6.6          | 0.09              |

TABLE III

VALUES OF THE CONCENTRATION EFFECT ( $\Delta$ ) FOR DIFFERENT CLASSES OF CHEMICAL SUBSTANCES (kcal/mole)

| <i>Chemical class</i>     |         |
|---------------------------|---------|
| Alcohols                  | 2.5-3.2 |
| Aliphatic nitro-compounds | 2.0     |
| Chloroalkanes             | 0.7-1.1 |
| Bromoalkanes              | 0.6-0.8 |
| Ketones                   | 0.8     |
| Aldehydes                 | 0.7     |

of chemical classes of substances on the basis of their ability to associate: alcohols, nitro-compounds, halogen compounds, ketones, aldehydes, nitriles, ethers. The concentration effect is very small for nitriles and ethers. The concentration effect of alcohols depends on the shielding of the hydroxyl groups by hydrocarbon radicals: it decreases from *n*-alcohols to *tert.*-alcohols. The changes in the values of  $\Delta$  for other isomeric compounds are very small. For example, the values of  $\Delta$  of the chloroalkanes are changed only by 0.1-0.2 kcal. The concentration effect is negligible when the polar atomic groups are shielded. For example, carbon tetrachloride and *tert.*-butyl chloride have very small  $\Delta$  values.

The experimental results obtained allows one to draw some conclusions concerning the calculation of the heats of solution of polar solutes in non-polar stationary phases. The value of the concentration effect decreases rapidly in the first members of an homologous series and is then stabilised. The possible  $\Sigma$  values of different chemical classes of substances are listed in Table III. These values allow the calculation of heats of solution for polar solutes in non-polar solvents in GLC.

Naturally, a change in the amount of stationary phase and in the length of the column varies the retention values of polar solutes in non-polar stationary phases. Therefore it is recommended that the stable experimental conditions are maintained for the comparison of calculated and experimental heats of solution of the substances under study.

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