

CONTRIBUTION TO THE MOLECULAR THEORY OF SOLUTIONS IN GAS-LIQUID CHROMATOGRAPHY

SHAPE AND SYMMETRY OF MOLECULES

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The use of physical concepts and, in particular, the methods of theoretical physics, usually leads to very fruitful results in determining the selectivity of the stationary phase in gas-liquid chromatography. However, the application of these methods to real solutions of organic compounds is restricted by a number of simplifying assumptions which are employed in studies in theoretical physics. One of these assumptions is the calculation of intermolecular interactions for a system of spherical particles. These are justified for liquids similar to noble gases. However, the shape of many organic molecules deviates greatly from spherical. Therefore, when calculating the intermolecular interactions it is useful to consider the relationships between the thermodynamics of the solutions of organic compounds and their shape and symmetry. Such relationships will allow the use of the basic principles and the formulae derived for spherical particles in molecular physics and for solutions of particles of non-spherical shape. In the present paper an attempt will be made to establish relations between the elementary characteristics of molecules (polarizability, Van der Waals radius) and the potential energy of dispersion interaction in gas-chromatographic solutions of molecules of different shape.

Let us consider a dispersion interaction of the atoms in molecules of organic substances with a continuous environment of stationary phase. This means that molecules of stationary phase change their conformation so as to provide an optimal interaction for all the atoms of the solute molecules.

A sufficiently good approach for such a system is the solution of a low molecular *n*-paraffin in a high molecular *n*-paraffin. The second assumption consists in that the carbon atoms are considered as a whole with the surrounding hydrogen atoms. This assumption may be justified by the small size of the hydrogen atom compared to carbon atoms. And, finally, the interaction of a solute molecule with the environment is taken to be equal to the sum of interactions of all the atoms in this molecule. Then the dispersion interaction can be described by LONDON's formula:

$$U = \frac{3}{2} \frac{I_1 + I_2}{I_1 I_2} \frac{a_1 a_2}{r^6} \quad (1)$$

where U = dispersion energy;

I = ionization potential;

a = polarizability;

r = interatomic distance; subscript 1 refers to the solute and subscript 2 to the environment.

The ionization potentials of hydrocarbons and their halogen derivatives do not differ greatly from each other and substitution of these values in eqn. (1) decreases the difference further. Therefore, in the first approximation it is possible to neglect the difference in the ionization potentials of the substances being compared. Then eqn. (1) can be simplified as follows:

$$D = \frac{a_1 a_2}{r^6} \quad (2)$$

The interatomic distances are assumed equal to the sum of the Van der Waals radii. In real liquids the interatomic distances exceed the sum of the Van der Waals radii and depend on the temperature. This approximation is justified by the fact that for comparative calculations it is possible to consider the same relation between the optimal distances and the Van der Waals radii at one and the same temperature. The constant multiple does not change the relation between the quantities.

And, finally, to simplify the calculations let us assume that every atom of a solute molecule interacts with one methylene group of the environment. Then, one can calculate the relative values of dispersion interaction for any atom of a solute with the environment, by substituting in eqn. (2) the refraction of atoms (or groups of atoms if hydrogen is present) for the polarizability and the sum of Van der Waals radii.

The determinations are simply carried out for a number of nonpolar solvents when the electrostatic forces in the intermolecular interactions can be neglected. In this case it is possible to connect the basic energy values with the change in shape and symmetry of the solute molecules for controlled values of the remaining parameters. From the practical standpoint the following liquids were selected: *n*-pentadecane, squalane, bicyclohexyl and 1,3-dimethylnaphthalene. The first three liquids differ only in their structure. The structure of liquid pentadecane is formed by isotactic linear hydrocarbon chains of molecules. A regular lattice is typical for this liquid, however, concentration effects of solubility are considerable in this case¹. Such effects influence first of all the solubility of polar substances, which is connected with the possibility of association of the solute molecules in the solvent environment. Association is facilitated by decreasing the impediments to the motion of the solute molecules in the holes between the solvent molecules. In squalane secondary methyl groups hinder such motion, leading to a reduction of concentration effects. Bicyclohexyl constitutes a system of ring molecules each of which lies on top of the other with a small displacement so as to form close packing. The intermolecular holes in such liquids are bounded by rectangular areas unlike the cylindrical holes in *n*-paraffins. The concentration effects are minimal for such a stationary phase. 1,3-Dimethylnaphthalene has a coplanar arrangement. These molecules have an easily polarizable aromatic ring with a variable density of the electron cloud.

As solutes, a series of methane derivatives have been chosen, obtained by substitution of hydrogen atoms by chlorine or bromine atoms. In this way it is possible to connect the properties of molecules of different shapes. The ideal case would be to choose nonpolar molecules having the same polarizability. However, in reality, the

derivatives obtained in this manner possess different polarizability and unequal dipole moments. This circumstance leads to a number of reservations in considering the dispersion forces, which are due to the different induction forces and concentration effects.

As a nonpolar solute for all atoms for which it is possible to realize optimum interaction, *n*-hexane may be used. Then, on the basis of the index of dispersion interaction *D*, the heat of solution can be calculated for other substances as follows:

$$D_0 = \frac{H_s}{D}$$

The subscript 0 indicates the value of the heat of solution per unit dispersion interaction of *n*-hexane. However, such calculated data disagree with experimental values obtained for molecules of different shape (Table I).

TABLE I

CALCULATED AND EXPERIMENTAL VALUES OF HEATS OF SOLUTION IN PENTADECANE AT 50° (kcal per mole)

1 = Experimental value; 2 = calculated without correlation; 4 = calculated with correlation; 3, 5 = error.

Component	1	2	3	4	5
Carbon tetrachloride	8.3	9.4	—1.0	8.9	—0.6
1,1,1-Trichloroethane	8.1	8.6	—0.4	8.3	—0.2
2,2-Dichloropropane	7.1	8.0	—0.9	7.7	—0.6
<i>tert.</i> -Butyl chloride	6.9	7.4	—0.5	7.2	—0.3
Chloroform	7.6	7.4	0.2	7.4	0.2
1,1-Dichloroethane	7.1	6.8	0.3	6.8	0.3
Isopropyl bromide	7.5	6.4	1.1	6.6	0.9
Ethyl bromide	6.3	5.3	1.0	5.7	0.6

The calculations were made using eqn. (2), the methylene group (refraction 4.6 units; Van der Waals radius 20 Å) having been taken as environment for each atom of the solute molecule. The experimental deviations are about 0.1 kcal per mole. The experimental values of the heats of solution were calculated on the basis of the retention volumes in a manner described in ref. 2.

The discrepancies between the calculated and experimental values lead to the assumption that not all like atoms of the solute molecule make an equal contribution to the value of the intermolecular forces. Indeed, eqn. (2) has been derived for particles with a spherical field of action. In polyatomic molecules this principle cannot be realized, since the adjacent atoms prevent contact with the environment. For example, a chlorine atom in a molecule of carbon tetrachloride is shielded on the side by the radical —CCl₃. If on the most accessible, external side of the molecule the Van der Waals radius of chlorine is equal to 1.85 Å, then on the opposite side it will be 3.6 Å (Fig. 1). Therefore, for real systems a correction should be introduced for so-called shielding of atoms by a neighbouring radical.

A detailed computation of the shielding effect is very complicated mathematically, therefore we shall introduce the following simplifying assumptions: a chlorine

atom (methyl group) is shielded by the neighbouring methyl group (chlorine atom) by $1/4$ (because in a molecule of carbon tetrachloride the central carbon atom is almost entirely, 93 %, shielded by the chlorine atoms). The radical $-\text{CCl}_3$ shields the neighbouring atom to a somewhat greater extent: by $1/3$. In this manner it is

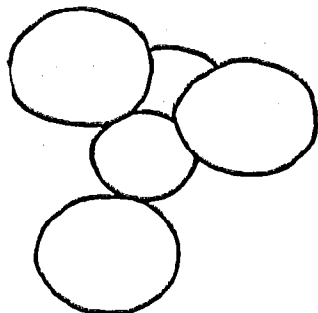


Fig. 1. Carbon tetrachloride molecule.

possible to calculate the indexes of dispersion interaction for the molecules under consideration (Table II).

Table I gives the values of heats of solution calculated on the basis of the dispersion interaction indexes as contained in Table II. It is seen that the discrepancies are decreased, confirming the above assumptions on shielding.

TABLE II

INDEXES OF DISPERSION INTERACTION FOR THE MOLECULES UNDER INVESTIGATION (IN CONVENTIONAL UNITS)

Substance	Atom groups and their <i>D</i>						Sum of <i>D</i>
Carbon tetrachloride	C	0.4	4 Cl	6.0			24.4
1,1,1-Trichloroethane	C	0.4	3 Cl	6.0	CH ₃	4.4	22.2
2,2-Dichloropropane	C	0.4	2 Cl	6.0	2 CH ₃	4.4	21.1
<i>tert.</i> -Butyl chloride	C	0.4	Cl	6.0	3 CH ₃	4.4	19.6
Hexane			3 CH ₃	5.0	4 CH ₂	2.8	21.2
Chloroform			CH	1.3	3 Cl	6.3	20.3
1,1-Dichloroethane	CH	1.3	2 Cl	6.3	CH ₃	4.6	18.5
Isopropyl bromide	CH	1.3	Br	7.5	2 CH ₃	4.6	18.0
Ethyl bromide	CH ₂	2.8	Br	7.8	CH ₃	5.0	15.6

Since the symmetry of an organic molecule is directly connected with the degree of shielding, the connection between the symmetry of an organic substance and its heat of solution becomes clear. The higher the symmetry of the molecule (with constant polarizability), the greater the effect of shielding on its interaction with the environment. Thus, for instance, in a carbon tetrachloride molecule a carbon atom is practically fully shielded by the chlorine atoms, while the chlorine atoms are also shielded by the radicals $-\text{CCl}_3$. The degree of shielding is lowered on transition to a more unsymmetrical form (for example, to linear *n*-paraffin chains). This effect is one of the reasons why the heats of solution of symmetrical molecules are lower than in the case of unsymmetrical molecules.

The change in the entropy of solution for molecules of similar dimensions consists of two main parts: the entropy of the molecule mass centre translation and the

rotation entropy. The first component is associated with the heat of solution, while the second component reflects the change in the rotational degrees of freedom on going into solution. Since the translational entropy is a function of the heat of solution, the rotation entropy will characterize the solution entropy as an independent variable³.

The translational entropy is found as the product of the heat of solution taken with the reverse sign by the factor of proportionality depending on the temperature. For example, the numerical value of this factor is equal to $2.6 \cdot 10^{-3}$ at 50° . The rotation entropy is determined as the difference between the solution entropy and the translational entropy. Such relative values of the rotation entropy (with carbon tetrachloride taken as standard) are given in Table III.

TABLE III

CHANGE IN ROTATION ENTROPY DURING SOLUTION (E.U.)

Component	Stationary phase*				
	1	2	3	4	5
1,1,1-Trichloroethane	-0.4	-0.4			0.4
2,2-Dichloropropane	-0.4	-0.4	-0.4	-0.1	0.4
Chloroform	-1.0	-0.7	-0.6	-0.7	1.5
1,1-Dichloroethane	-1.4	-1.1	-1.0	-0.8	0.4
Isopropyl bromide	-1.4	-0.8	-0.8	-0.8	-0.4
Ethyl bromide	-1.8	-1.6	-2.0	-1.7	-0.6

* 1 = pentadecane; 2 = squalane; 3 = bicyclohexyl; 4 = 1,3-dimethylnaphthalene; 5 = oxydipropionitrile.

A carbon tetrachloride molecule has 3 axes of rotation of the third order and 3 axes of the second order. The remaining spherical molecules (1,1,1-trichloroethane, 2,2-dichloropropane) do not possess such high symmetry. Experimental results show that the greatest hindrance is experienced by molecules having a lower degree of symmetry. The same can be shown to exist also for the trisubstituted derivatives of methane. For 1,1-dichloroethane which has no axes of symmetry the rotation entropy is decreased in comparison with chloroform.

However, the number of axes of symmetry of different orders is not a sufficiently exhaustive characteristic of a molecule in estimating the change in rotation entropy. In this case the shape of the molecule as estimated by its Van der Waals radius is of great importance. From this point of view it is possible to compare tetra-, tri- and di-substituted derivatives of methane. For instance, 1,1,1-trichloroethane and chloroform possess one axis of symmetry of the third order, but the difference in the shape of the molecule leads to decreased rotation entropy of chloroform. The same can be also said concerning the 1,1-dichloroethane and ethyl bromide pair.

Consequently, increasing the symmetry of the molecule and its approach to spherical shape raise the rotation entropy of solution in a nonpolar solvent. The substitution of a methyl group (or one equal in size) for each hydrogen atom in methane lowers the rotation entropy in a nonpolar solvent approximately by 0.5 e.u. (for molecules with the same degree of symmetry). Decreasing the number of axes of symmetry

of the third order by one or two units for molecules of the same shape lowers the rotation entropy approximately by 0.4 e.u. in nonpolar solvent.

By analyzing the thermodynamic functions of solution in a continuous nonpolar environment, it is possible to state that increasing the degree of symmetry of the molecule and its approach to spherical shape lowers the solution heat and raises the rotation entropy. These two effects act upon the retention volume with different signs. For the systems under investigation, the fall in the heat of solution is of greater significance in the formation of the retention volume than the entropy.

Comparison of nonpolar solvents

Table IV contains the differences between the experimental and calculated heats of solution in different nonpolar solvents. A negative value for the differences for the tetrasubstituted derivatives of methane may be indicated as a general rule.

TABLE IV

DIFFERENCES OF CALCULATED AND EXPERIMENTAL VALUES OF HEATS OF SOLUTION (kcal per mole)

Component	Stationary phase*				
	1	2	3	4	5
Carbon tetrachloride	-0.5	-0.7	-0.2	-0.9	-1.4
1,1,1-Trichloroethane	-0.2	-0.2			-1.0
1,1-Dichloroethane	0.3	-0.1	-0.2	1.0	1.3
Ethyl bromide	0.6	0	0.8	1.5	1.2

* For numbers 1 to 5, see Table III.

This is essentially a correction for the discontinuity of the environment: the large spherical molecules cannot be arranged in the stationary phase in such a manner as to ensure optimum interaction with it and all the atoms of the solute molecule. For instance, a real *n*-paraffin chain cannot bend so as to provide contact with all the atoms of chlorine. Therefore, the value of the difference between the calculated and experimental heats of solution for large spherical molecules may serve as a characteristic for the deformation of the molecules of the stationary phase, *i.e.* for the plasticity of the environment. Among the stationary phases investigated, bicyclohexyl possesses the highest plasticity. This is followed by squalane and pentadecane with almost equal plasticity and, finally, dimethylnaphthalene, as is readily explained by comparing the molecular structures of these liquids. Bicyclohexyl molecules have a bent conformation, different space isomers being possible for this substance. The latter circumstance increases the probability of filling any point of the environment with atom groups of the stationary phase. By contrast, the coplanar arrangement of planar dimethylnaphthalene molecules brings about a regular arrangement of the atoms in space, which lowers the solution heat of the spherical molecules. Saturated hydrocarbons (pentadecane, squalane) occupy an intermediate position.

In this manner, on the basis of the difference between the calculated and experimental heats of solution of spherical molecules the so-called plasticity of nonpolar solvents can be estimated. This parameter characterizes the probability of finding methylene groups of the solvent in any elementary volume of the environment.

The rotation entropy is more sensitive to the tightness of packing of the liquid. The more closely the particles of the stationary phase are packed, the greater is the drop of the rotation energy of the molecules which do not possess a high degree of symmetry (compared to symmetrical molecules).

In this connection, it is possible to judge the change in the tightness of packing of the liquid by the change of the rotation entropy for different molecules. From experimental results (Table III) it may be concluded that only *n*-pentadecane stands out among the remaining hydrocarbon solvents owing to the low values of the rotation entropy of nonsymmetrical molecules. This is aided by the regular orderly arrangement of its carbon chains.

Effect of the shape and symmetry of molecules on the thermodynamics of solution in a polar stationary phase

In Tables III and IV the experimental results are given on the thermodynamics of solution in a polar stationary phase oxydipropionitrile. The use of the difference between the calculated and experimental heats of solution as a criterion of the plasticity of the stationary phase is applied to polar liquids. It is natural to expect that the structure of polar liquids is more ordered at the expense of the strong bonds between the polar groupings of atoms. Indeed, the plasticity index of the stationary phase for oxydipropionitrile is minimum (as judged only by the nonpolar carbon tetrachloride). Consequently, the plasticity of the stationary phase can be estimated also for polar liquids, using the procedure described above.

The change in rotation entropy during solution of molecules in nonpolar solvents first of all characterizes the symmetry of the molecule itself. A molecule with a great number of degrees of freedom and a more symmetrical shape possesses a high rotation entropy in such a solution. The polar strongly associated liquid with a hard structure acts in a different manner: in this case the small values of the intermolecular distances exert an influence (usually, more polar liquids have a higher density). Rotation of the molecules in the environment of the stationary phase is then hindered in such a manner that relatively greater hindrance is experienced by more symmetrical molecules. In other words, hindrance according to the degrees of freedom of rotation begins to play an essential part. This effect becomes obvious on comparing the data, contained in Table III. For instance, the more symmetrical carbon tetrachloride is hindered to a greater degree than 1,1,1-trichloroethane.

If in solutions of nonpolar solvents the increasing degree of symmetry and the approach of the molecule to spherical shape reduces the retention volume mainly at the expense of the intermolecular forces, in polar solvents the rotation entropy does not affect the retention volume in the same manner. Therefore, the relative decrease of the retention volume for spherical molecules is more clearly seen in polar than in nonpolar solvents.

SUMMARY

The relations between the shape of molecules and their thermodynamical functions of solutions were studied. It was shown that the effect of shielding of the centre of the molecule is the most important factor in the heat of solution. The entropy of solution is connected with the shape of the molecules in a different manner.

The differences between the experimental and calculated heats of solution of spherical molecules are a measure of the plasticity of the stationary phase.

REFERENCES

- 1 A. N. KOROL, *Ukr. Chem. J.*, 32 (1966) 329.
- 2 D. H. DESTY AND W. T. SWANTON, *J. Phys. Chem.*, 65 (1961) 766.
- 3 A. N. KOROL, *Exptl. Theor. Chem. (USSR)*, 1 (1965) 769.

J. Chromatog., 25 (1966) 252-259