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INTERPRETATION OF GAS CHROMATOGRAPHIC DATA

HYDROCARBONS AND AROMATIC COMPOUNDS ON CARBOWAX 400*

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SUMMARY

The behaviour of aliphatic hydrocarbons and aromatic compounds was studied on squalane and on polyethyleneglycol (Carbowax 400).

Activity coefficients and determinations of excess thermodynamic functions allow the authors to interpret the retention data, on a thermodynamic basis, from a qualitative point of view.

INTRODUCTION

The gas–liquid chromatographic process relies on the establishment of a continuous series of evaporation and dissolution stages involving the sample and a solvent on a support. It seems therefore profitable to study the chromatographic behaviour of substances on the basis of the thermodynamics of solutions.

Measurement of the activity coefficients and calculation of the thermodynamic excess functions give useful information on the nature of the intermolecular forces which operate in the solution and determine the elution. It is in this way that we shall now interpret the gas chromatographic results obtained with alkanes and aromatic compounds on Carbowax 400 and squalane.

The activity coefficients γ for the solutes at 58°, 78°, and 88°C were obtained from the specific retention volumes V_g with the aid of the formula[1]

$$\gamma = \frac{1.7 \times 10^7}{M_L \cdot p^\circ \cdot V_g} \quad (1)$$

where M_L is the molecular weight of the stationary phase and p° is the vapour pressure of the solute at temperature T. The activity coefficient gives the deviation from Raoult's law and—since the vapour pressure is used instead of the fugacity—it also gives the deviation from ideality in the solution and the gas phase. Eqn. (1) has recently been used by MARTIRE[2] in his thermodynamic study on dilute solutions. This author also specified the conditions needed to obtain significant results[3], and these

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conditions were used in the present work. The activity coefficient of a solute is connected with the excess partial molar free energy $\Delta\mu^E$ by the equation:

$$\Delta\mu^E = RT \ln \gamma \tag{2}$$

Furthermore, since

$$\Delta\mu = \Delta h^E - T\Delta s^E \tag{3}$$

we obtain

$$\ln \gamma = \frac{\Delta h^E}{RT} - \frac{\Delta s^E}{R} \tag{4}$$

where Δh^E and Δs^E are the excess partial molar enthalpy and entropy, respectively. It should theoretically be possible to determine these quantities by gas chromatography, but experimental errors cannot be eliminated even in accurate work. It is possible, on the other hand, to compare the values within a given series, these values all exhibiting the same error[4,5].

The deviations from Raoult's law are due to differences between the molecular volume of the solute and that of the solvent, and to differences between the intermolecular forces in the solution and those in the pure liquid. The first type of difference, making a positive contribution to the excess entropy, is particularly important in GLC. Differences of the second type apply to all solutions, the resulting contributions being either positive or negative.

By adopting, for binary solutions, a simplified lattice model, the following proportionality relationship between partial molar excess enthalpy and energies of interaction between solution components, was obtained[6]:

$$\Delta h^E \propto (\tfrac{1}{2}W_{AA} + \tfrac{1}{2}W_{BB} - W_{AB}) \tag{5}$$

where the W terms denote the absolute values of the energies of interaction between two molecules of solvent (W_{AA}), two molecules of solute (W_{BB}), and one molecule of each (W_{AB})[6].

This model of solutions, with the same results for the partial molar excess enthalpy, was applied also to solutions of molecules of different size[6].

The same model for binary solutions was assumed by MARTIRE AND POLLARA[3] for the interpretation of gas chromatographic data concerning aromatic hydrocarbons on squalane. Later, MARTIRE applied HILDEBRAND's interpretation for regular solutions to aliphatic hydrocarbons in di-*n*-butyl phthalate[2].

The relation (5), together with the factors affecting the term Δs^E (eqn. 4), will be used for the interpretation of our experimental data. The main factors which characterise the gas chromatographic behaviour of the solutes examined, will be considered separately.

EXPERIMENTAL

We used a Fractovap GV (ex C. Erba, Milan), fitted with a thermal conductivity detector and a 2 m steel column (I.D. 6 mm). The stationary phase was Carbowax 400 or squalane (ex C. Erba) in a quantity of 20 % on 60–80 mesh silanized Chromosorb P. The samples (*cf.* Tables I and II) were obtained from C. Erba (Milan), B.D.H. (London) and Merck (Darmstadt), and were used without further purification. The

TABLE I

	V_g (*at 58°C*)	V_g (*at 78°C*)	V_g (*at 88°C*)	$\Delta H_E{}^S$ (*kcal/mole*)
n-Hexane	8.5	5.6	4.4	5.0
n-Heptane	18.6	11.0	8.6	6.1
n-Octane	38.8	21.4	16.0	7.0
n-Nonane	80.2	40.5	29.4	7.9
n-Decane	165.0	76.1	53.3	8.9
Cyclohexane	24.8	15.2	12.0	5.7

TABLE II

	V_g (*at 58°C*)	V_g (*at 78°C*)	V_g (*at 88°C*)	$\Delta H_E{}^S$ (*kcal/mole*)
o-Xylene	684	310	218	9.0
m-Xylene	508	234	166.7	8.8
p-Xylene	486	225	160.1	8.8
Toluene	258	127.4	91.3	8.2
Benzene	131.6	68.9	50.7	7.5
Chlorobenzene	842	375	259	9.3
Fluorobenzene	178.5	89.8	64.1	8.0
Thiophen	231	115.5	82.8	8.1

temperature was set at 58°, 78°, or 88°C, and was checked with a platinum resistance pyrometer, whose resistance was measured with a differential Wheatstone bridge. The sample was introduced with a Hamilton microsyringe in an amount of 0.5 μl. This was accompanied by the simultaneous introduction of a small amount of air. The flow rate of the carrier helium was about 1 ml/sec (for 0°C and 760 mm Hg). The gas pressure at the column inlet was measured with a differential mercury manometer, the outlet pressure (atmospheric) being checked with a Fortin barometer. The retention time (*i.e.* the distance between the maximum of the sample peak and that of the air peak) was measured with a stop-watch to make the values more accurate and independent of possible anomalies in the chart speed. The calculation and the presentation of the V_g values conform to the IUPAC recommendations[7] (see Tables I and II).

The variation of V_g with the temperature is given by

$$\log V_g = \frac{K_1 \times 10^3}{T} + K_2 \tag{6}$$

The values of the constants K_1 and K_2, calculated by the least-squares method, are listed in Table III. The same variation can also be expressed as

$$\log V_g = \frac{\Delta H_E{}^S}{2.3RT} + K_2 \tag{7}$$

Combination of eqns. (6) and (7) permits the calculation of the differential molar heat of vaporization from the stationary phase:

$$\Delta H_E{}^S = K_1 \times 2.3R \text{ (kcal/mole)}$$

where $R = 1.98$ cal/degK.mole.

The values of the activity coefficient were calculated with eqn. (1), while Antoine's equations, whose constants are given in refs. 8–10, were used to find the values of $p°$. We found $\Delta\mu^E$ from eqn. (2), and Δh^E and Δs^E from eqn. (3) and $\ln\gamma$. The results are shown in Tables V–VII.

TABLE III

	K_1	$-K_2$
n-Hexane	1.09676	2.38160
n-Heptane	1.33104	2.75056
n-Octane	1.52659	3.02235
n-Nonane	1.73448	3.33539
n-Decane	1.95288	3.68281
Cyclohexane	1.24661	2.37007
o-Xylene	1.97007	3.11689
m-Xylene	1.92659	3.11486
p-Xylene	1.91699	3.10475
Toluene	1.79454	3.00839
Benzene	1.63316	2.81618
Chlorobenzene	2.03428	3.22002
Fluorobenzene	1.75986	3.06461
Thiophen	1.76977	2.98180

DISCUSSION

1. Hydrocarbons on squalane

The results are listed in Table IV, together with the activity coefficients obtained by KWANTES AND RIJNDERS[11] and those deduced from V_g values by LITTLEWOOD[12]. Though our V_g values refer to 78°C and the data from refs. 11 and 12 to 80°C, comparison is admissible, because only a small variation in γ is expected in this narrow interval. The present values agree well with those of LITTLEWOOD, but these two sets differ from the values obtained by KWANTES AND RIJNDERS, such differences having been observed before[2].

According to MARTIRE[3], the chromatographic behaviour of alkanes can be explained by the statistical theory. Fig. 1 shows the increase in $\Delta\mu^E$ at 78°C with the number of carbon atoms. In the case of the benzene–cyclohexane pair, however, a comparison of the molecular volumes indicates that the γ values cannot be explained by the statistical theory. MARTIRE[3] has attributed this to a loss in the cohesive energy

TABLE IV

	V_g *(at 78°C)*	γ	γ *(ref. 11)*	γ *(ref. 12)*	$\Delta\mu^E$	*Molecular volume at 20°C (ml/mole)*
Benzene	98.3	0.58	0.59	0.57	−0.38	88.9
Toluene	247	0.60	0.61	0.58	−0.36	106.3
Cyclohexane	122.0	0.47	0.52	0.47	−0.52	108.1
n-Pentane	28.8	0.53	0.67	0.56	−0.44	115.2
n-Hexane	68.5	0.58	0.66	0.59	−0.37	131.6
n-Heptane	164.3	0.61	0.68	0.63	−0.34	146.5

in benzene, which makes a positive contribution to $\Delta\mu^E$. The difference between cyclohexane and toluene is still greater, for there appears here in addition a statistical effect caused by the larger molecular dimensions of toluene in comparison with benzene. The fact that γ is smaller for cyclohexane than for *n*-pentane and its higher homologues is to be ascribed to its small molecular volume.

2. *Alkanes on Carbowax 400*

In the calculation of the activity coefficients, a molecular weight of 409 was assumed[13] for Carbowax 400. The error introduced by this choice influences equally all the Δs^E values, so it does not affect a discussion in which the values are compared amongst themselves, instead of being given as absolute quantities. Table V shows that all the compounds exhibit marked positive deviations from Raoult's law. Furthermore the increase in $\Delta\mu^E$ with the number of carbon atoms is more pronounced with Carbowax 400 than with squalane as the stationary phase (*cf.* Fig. 1).

TABLE V

	γ			$\Delta\mu^E$ *kcal/mole*			Δh^E (*kcal/mole*)	Δs^E (*e.u.*)	$a = \Delta H_E{}^S/\Delta H^v$
	58°C	*78°C*	*88°C*	*58°C*	*78°C*	*88°C*			
n-Hexane	9.1	7.4	7.0	1.45	1.39	1.39	2.0	1.7	0.71
n-Heptane	11.5	9.4	8.7	1.60	1.56	1.55	2.1	1.5	0.74
n-Octane	14.9	12.0	11.1	1.77	1.73	1.73	2.2	1.3	0.75
n-Nonane	17.5	15.4	14.1	1.88	1.90	1.90	2.2	0.9	0.76
n-Decane	24.7	19.7	17.9	2.11	2.08	2.07	2.5	1.2	0.78
Cyclohexane	4.6	3.9	3.7	1.00	0.95	0.93	1.7	2.1	0.76

With some exceptions, Δh^E increases and Δs^E decreases with increasing number of carbon atoms in the present series, the exceptions being due to the experimental error involved. Inspection of eqn. (4) shows that positive Δh^E gives a high γ, while positive Δs^E detracts from the value of γ, and the observed increase in γ up the homologous series may be due either to increasing Δh^E or to decreasing Δs^E.

Positive Δh^E can indicate that $W_{AB} < 1/2(W_{AA} + W_{BB})$ and the observed increase in Δh^E suggests that this difference becomes more pronounced as the number of carbon atoms in the molecule increases. Positive Δs^E indicates that the partial molar entropy of the mixture is higher than in the ideal case, which is connected with the difference between the solvent and the solute as regards their molecular volumes. Since this difference decreases as the length of the alkane chain increases, the negative contribution of the entropy term to the activity coefficient becomes progressively smaller.

According to PIEROTTI *et al.*[14], the change in γ with the number of carbons in *n*-alkanes in polar solvents is due to changes in the interactions between the solute (R) and the polar groups of the solvent (X_1 = end OH or –O–) and between the solute and the paraffinic moiety of the solvent (R_1). The first interaction is proportional to the number of carbon atoms in R(n), *i.e.* it is given by K_3n, where K_3 is a constant. The R–R$_1$ interaction can be expressed by $K_4(n-n_1)^2$, where K_4 is a constant and n_1 is the number of carbons in the solvent. Since the activity coefficient is a measure of the solvent–solute interaction, and since there is a logarithmic relationship between them

$$\log \gamma = \text{constant} + K_3 n + K_4 (n - n_1)^2$$

The empirical function that can be deduced from Fig. 1 is linear and has the equation:

$$\log \gamma = A + Bn$$

where A and B are constants. It follows that K_4 can be neglected, so that R–X_1 is the only important interaction. It may thus be concluded that the order of elution of alkanes on Carbowax 400 is determined mainly by variations in the inductive forces between the solvent and the solute, the methylene groups of the stationary phase exerting only a small influence.

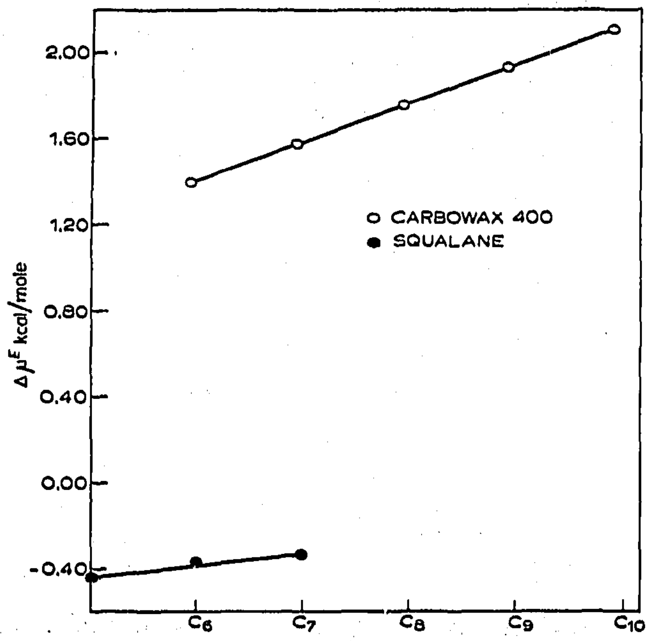

Fig. 1. Incremental relation between excess free energy and molecular structure for *n*-alkanes in Carbowax 400 and Squalane at 78°C.

The observed characteristics of the thermodynamic functions may also be deduced by considering the following equation for V_g as a function of the vapour pressure, verified by HOARE AND PURNELL[15]

$$\log V_g = -a \log p^\circ + \log \frac{1.7 \times 10^7}{\gamma_a M_L} + c(a - 1)$$

where γ_a, the athermic activity coefficient, is given by

$$\ln \gamma_a = -\frac{\Delta s^E}{R}$$

and a is the ratio between the differential molar heat of vaporization from the solution ($\Delta H_E{}^S$) and the molar enthalpy of vaporization of the pure solvent (ΔH^v). Table V shows that the values of a, found from the variation of $\log V_g$ with $\log p^\circ$, are all smaller than unity for alkanes and are in agreement with the positive value of $\Delta h^E (= \Delta H^v - \Delta H_E{}^S)$.

The same regularity is observed on examining thermodynamic parameters of closer chromatographic significance, such as the retention volume. The values of $\Delta H_E{}^S$ in Table II have been found from eqn. (7) giving the connection between V_g

and T. The values of ΔH^v for a series of alkanes regularly increase with the number of carbon atoms, and so do the values of Δh^E. Therefore $\Delta H_E{}^S$ also increases linearly with the number of carbons.

As on squalane, cyclohexane chromatographed on Carbowax 400 has a higher retention volume and a smaller activity coefficient than *n*-hexane, which may be due to the entropy term and hence to the difference in the molecular volumes (*cf.* Table IV). However, a more detailed interpretation is not possible on the basis of these values alone.

3. *Aromatic compounds and thiophen on Carbowax 400*

Table VI shows that the behaviour of aromatic compounds on this stationary phase is such as to give low activity coefficients. The deviation from Raoult's law is positive for toluene and the xylenes, and negative for benzene and the halobenzenes.

TABLE VI

	γ			$\Delta\mu^E$ (*kcal/mole*)			Δh^E (*kcal/mole*)	Δs^E (*e.u.*)	$a = \Delta H_E{}^S/\Delta H^v$
	58°C	*78°C*	*88°C*	*58°C*	*78°C*	*88°C*			
o-Xylene	1.63	1.53	1.48	0.32	0.30	0.30	0.8	1.4	0.92
m-Xylene	1.82	1.70	1.63	0.39	0.37	0.35	0.8	1.2	0.91
p-Xylene	1.82	1.70	1.65	0.39	0.37	0.36	0.8	1.2	0.92
Toluene	1.26	1.20	1.20	0.15	0.13	0.13	0.3	0.5	0.96
Benzene	0.87	0.85	0.85	−0.09	−0.11	−0.12	0	0.3	0.98
Chlorobenzene	0.81	0.81	0.81	−0.14	−0.15	−0.15	−0.1	0	1.01
Fluorobenzene	0.75	0.75	0.77	−0.19	−0.20	−0.18	−0.3	−0.3	1.03
Thiophen	0.57	0.57	0.59	−0.37	−0.39	−0.38	−0.3	0.2	1.03

TABLE VII

	Molecular volume at 20°C (ml/mole)	Δs^E (*e.u.*)
Thiophen	79.0	0.2
Benzene	88.9	0.3
Fluorobenzene	94.0	−0.3
Chlorobenzene	101.8	0
Toluene	106.3	0.5
o-Xylene	120.3	1.4
m-Xylene	122.8	1.2
p-Xylene	123.3	1.2

In the pairs xylene–toluene, toluene–benzene, benzene–chlorobenzene, and chlorobenzene–fluorobenzene, the first component always has a higher activity coefficient than the second. The statistical theory alone cannot explain this, because Δs^E should be higher for benzene than for toluene and higher for toluene than for the xylenes (Table VII). The molecular volume increases in the order benzene < toluene < xylene. However, Δh^E is higher for the first component than for the second in all the above pairs, and becomes negative for the two halobenzenes. It might be thought that W_{AB} increases with respect to $\frac{1}{2}(W_{AA} + W_{BB})$ along the above series. However, the loss in cohesive energy decreases from xylene to toluene and then to benzene. On the other hand, there is a gain in the cohesive energy on passing from benzene to fluorobenzene via chlorobenzene, provided that the absolute values of the excess thermodynamic functions are correct. In any case, the solvent–solute interaction increases from the xylenes to fluorobenzene. The solvent exerts inductive and orientational forces on these solutes, and these forces can interact with the permanent dipole of chlorobenzene, fluorobenzene, *o*-xylene, *m* xylene, and toluene. In all aromatic compounds, the inductive forces can interact with the delocalized electrons of the nucleus. Compounds with methyl group(s), *i.e.* toluene and xylenes, deserve special mention. The paraffinic part causes a positive deviation from Raoult's law (*cf.* Table VI). It seems probable that the $+I$ effect of the methyl group is negligible, while it is logical to assume that the presence of this group explains the effect similar to that found in the *n*-alkanes. Moreover, if the $+I$ effect were decisive, there would be a more pronounced difference between the three xylenes. The inductive effects with dipole formation operate in *o*- and *m*-xylene, but cancel out in *p*-xylene. Halogens directly attached to the ring give rise to a dipole that is stronger than that with the methyl group and has an opposite charge ($-I$ effect). Furthermore, the mesomeric $+M$ effect imparts a partial double bond character to carbon–halogen bonds, particularly when the halogen is fluorine. These circumstances may lead to a stronger interaction between the sample and the stationary phase. The halogens attached to the aromatic ring thus operate in the opposite direction to the methyl group and they reduce the activity coefficient. The fact that Δh^E is small or negative for halobenzenes indicates a solvent–solute interaction stronger than in the case of benzene and its methyl derivatives. Decreasing Δh^E (sign of stronger solvent–solute interactions) is accompanied by a decrease in Δs^E (sign of ordering processes in the solution). This is shown in Fig. 2.

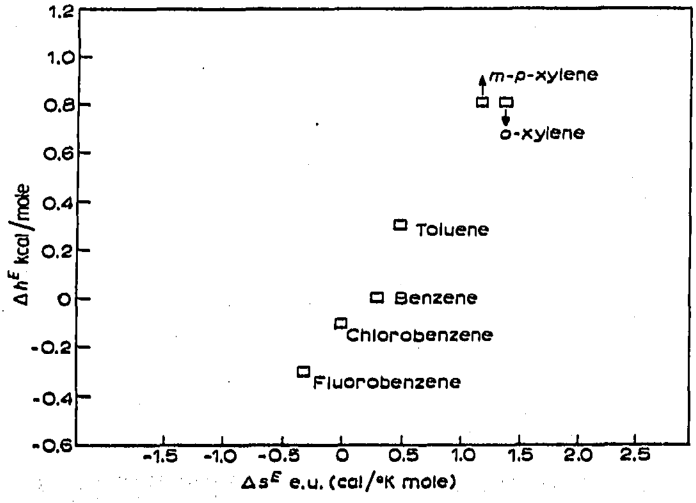

Fig. 2. Plot of Δh^E against Δs^E for aromatic compounds.

Since the forces involved are basically directional, this behaviour is to be expected.

The small differences between the three xylenes are not easy to explain, for the excess thermodynamic functions are too much alike to indicate any reason for them. The fact that *o*-xylene can be separated from a mixture of the three isomers on Carbowax 400 is due more to the difference in the vapour pressure than to the difference in the activity coefficients. The corresponding a values ($a = \Delta H_E{}^S/\Delta H^v$) agree with the Δh^E values obtained. The closeness of benzene and thiophen is due to the similarity between their behaviour.

Thiophen has lower γ values than benzene at all temperatures, which is due more to energetic than to entropy factors. The excess partial molar entropy is roughly the same for them despite the difference in the molecular volume, but the enthalpy values show a considerable difference. This suggests that the sulphur in thiophen gives rise to stronger orientational and inductive interactions.

CONCLUSIONS

There is a fundamental difference between Carbowax 400 and squalane as regards the retention of alkanes. The dispersive forces on squalane are such as to give rise to strong interactions with compounds that can exhibit mainly dispersive forces.

The chromatographic behaviour of alkanes on squalane is explained by the Flory-Huggins and the Guggenheim-Miller statistical theories, that of alkanes on Carbowax 400 being explained by the theory of Hildebrand and Scott. According to the latter, the strong positive deviations from Raoult's law are due to differences between the solvent–solvent, the solute–solute, and the solvent–solute interactions, while the statistical factor, though operative, plays a secondary part.

However, these theories do not take into account specific and directional interactions, and cannot therefore explain the chromatographic behaviour of aromatic compounds, which is determined by these interactions on Carbowax 400.

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