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AN INVESTIGATION INTO HYDROGEN BONDING IN GAS-LIQUID CHROMATOGRAPHY

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SUMMARY

Aromatic ketones and a nitroso compound, providing the oxygen donor atom for hydrogen bonding, have been studied. The energies of the spectroscopic solvent shifts of the donor molecules have been correlated with gas-liquid chromatographic retention index data when the donor molecules are used as the stationary phases. Linear relationships for both hydrogen bonding and non hydrogen bonding solvents have been established and hydrogen bonding energies for several systems are tabulated. The significance of the solute-solvent interactions between the ketones studied and chloroparaffins, alcohols and amines is discussed.

INTRODUCTION

That hydrogen bonding, when it occurs, is an important factor in retention in gas-liquid chromatography, is an accepted fact. The hydrogen bonding effect has been discussed by AMBROSE AND AMBROSE¹, PURNELL² and DAL NOGARE AND JUVET³ in general terms and compared with EWELL *et al.*'s⁴ classification scheme for hydrogen bonding in fractional distillation. Any study in solvent selectivity is made complex by the various forces which have to be considered, *i.e.* (a) dispersion forces which operate in all systems at all times, (b) orientation forces arising from the interaction of permanent dipoles, of which hydrogen bonding is an extreme case and (c) induction forces caused by the polarization of normally non-polar molecules when they are subjected to the field of a molecule having a permanent dipole. Solute-solvent systems showing a high degree of attraction, for instance ketone-alcohol systems, will demonstrate negative deviations from Raoult's Law — the solute being well retained by the solvent which can then be said to show high selectivity for the solute.

The Kováts⁵ retention index (I) is a parameter which can be used to study the extent of solute-solvent interactions in gas-liquid chromatography, ROHR-SCHNEIDER⁶ having used the index increment (ΔI) to describe the polarity of various stationary phases with respect to squalane. For a given solute, the index increment, $I_{\text{stationary phase}} - I_{\text{squalane}}$, is a measure of the solute-solvent interaction in terms of the orientation and induction forces described above. The quantitative interpretation of experimental results however, is virtually impossible at the present. Useful work

to overcome the difficulties has been carried out by SCHOMBURG⁷ by the use of "homomorphic factors" and by DIMOV AND SHOPOV⁸ using theoretical indices based on physical data such as molecular weight, vapour pressure and density. ROBINSON AND ODELL⁹ have proposed a Standard Retention Index calculated from boiling point data and TAKÁCS AND SZITA¹⁰ have developed an approximation method by which the retention index of a substance may be determined on the basis of its molecular structure.

However, one field from which a large amount of solute-solvent interaction data is available does not appear to have been studied in correlation with retention data. This is the UV spectroscopic behaviour of dilute solutions. In 1930 BURAWOY¹¹ observed that the $n \rightarrow \pi^*$ transition of a carbonyl compound moved to shorter wavelength as the solvent polarity increased, this increased amount of energy being associated with hydrogen bonding in hydroxylic solvents. BREALEY AND KASHA¹² have correlated blue shifts of the $n \rightarrow \pi^*$ band with hydrogen bond strengths, finding for benzophenone a blue shift of 1170 cm^{-1} between the two solvents hexane and ethyl alcohol. This shift they attribute to the hydrogen bond energy in the electronic ground state; non hydrogen bonding solvents giving blue shifts they attribute to preferential orientation of solvent molecules about benzophenone.

Iro *et al.*¹³ have studied ketone solutes with a wide range of solvents and concludes that the solvent induced blue shift in ketones is contributed to mainly by stabilization energy in the ground state, the magnitude of the shift representing stabilization energy in the ground state of the solute arising from its electrostatic and hydrogen bonding interactions with solvent molecules. BREALEY AND KASHA¹² obtained a value of 2.6 kcal/mole for the benzophenone-ethyl alcohol system by measurement of the blue shift and a value of 2.2 kcal/mole from IR data. LASCOMBE AND JOSIEN¹⁴ have measured the hydrogen bonding energy in the acetophenone-chloroform system by IR and KILP *et al.*¹⁵ have obtained a value for the benzophenone-chloroform system using dielectric data.

As the solvent shift is concerned with stabilization of the electronic ground state it should be possible to establish a relationship, for a particular solute-solvent system, between the spectroscopic shift of the $n \rightarrow \pi^*$ band on changing the solvent from hexane, and the retention increment, ΔI , on changing the stationary phase from squalane. For example taking benzophenone, the energy of hydrogen bonding between benzophenone and ethyl alcohol may be obtained from the difference between spectra of benzophenone in ethyl alcohol and in hexane. Using a stationary phase of benzophenone (liquid), the retention index of ethyl alcohol can be determined. The value of I for ethyl alcohol on a squalane column under identical conditions of temperature and gas flow may also be determined and ΔI for the system benzophenone-ethyl alcohol calculated. Using a series of solvents and species containing donor atoms (ketones), the relationship between ΔI and the spectroscopic shifts may then be examined. It is the result of this examination which is discussed in this paper.

EXPERIMENTAL

Donor compounds

Acetophenone, benzophenone, benzil, N-nitrosomethylaniline were used as donor compounds.

Solvents

The following solvents were used: benzene, diethyl ether, dichloromethane, chloroform, carbon tetrachloride, diethylamine, *tert.*-butylamine, ethyl alcohol, methyl alcohol.

All UV spectra were recorded on a Pye Unicam SP800 double-beam spectrophotometer using 1 cm silica cells. Aholmium filter, giving a sharp peak at 27,710 cm^{-1} , was used to calibrate the instrument.

Chromatographic data were obtained using a Pye 104 series gas chromatograph with flame ionization detector. Retention times were measured directly by stopwatch, corrected retention times were calculated from *m*-paraffin peaks by the method of PETERSON AND HIRSCH¹⁶.

Columns

A copper tubing (154 cm \times 0.6 cm O.D.) was packed with 10% w/w stationary phase on silylated Celite. For conditions of the column see Table II.

All solvents were chromatographed with the appropriate two *m*-paraffins, selected from the range *n*-hexane to *n*-nonane. The sample size was 1 μl . Retention indices were calculated from formula:

$$I = 100 \cdot \frac{\log t'_x - \log t'_{P_z}}{\log t'_{(P_z+1)} - \log t'_{P_z}} + 100_z$$

TABLE I

OPERATING CONDITIONS OF THE COLUMNS USED

Column	Operating temperature ($^{\circ}\text{C}$)	M.p. of stationary phase ($^{\circ}\text{C}$)	Nitrogen flow (ml/min)
Acetophenone	50	26	1.20
Benzophenone	50	48	1.20
Benzil	100	95	3.0
N-Nitrosomethylaniline	50	14.5	1.20
Squalane	50/100	—	1.20/3.0

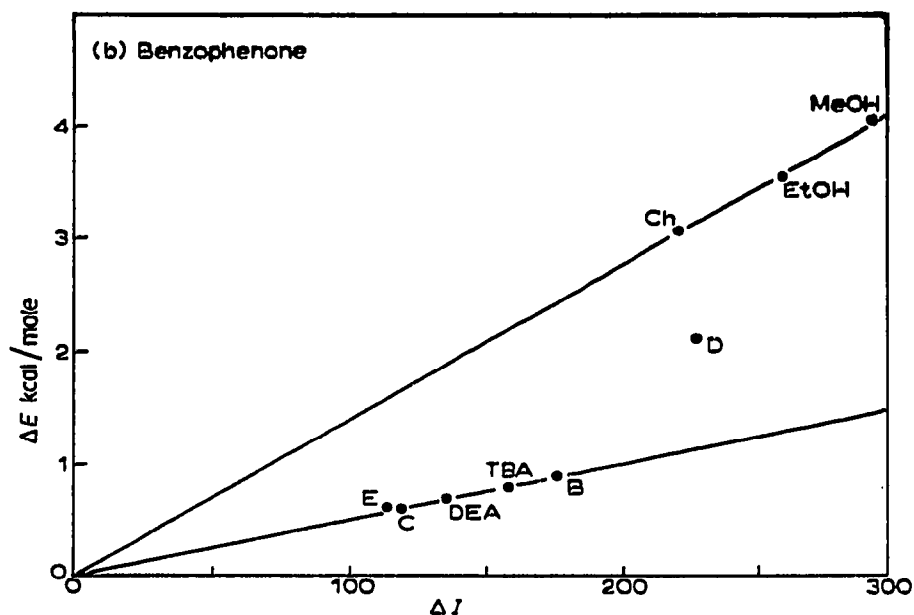
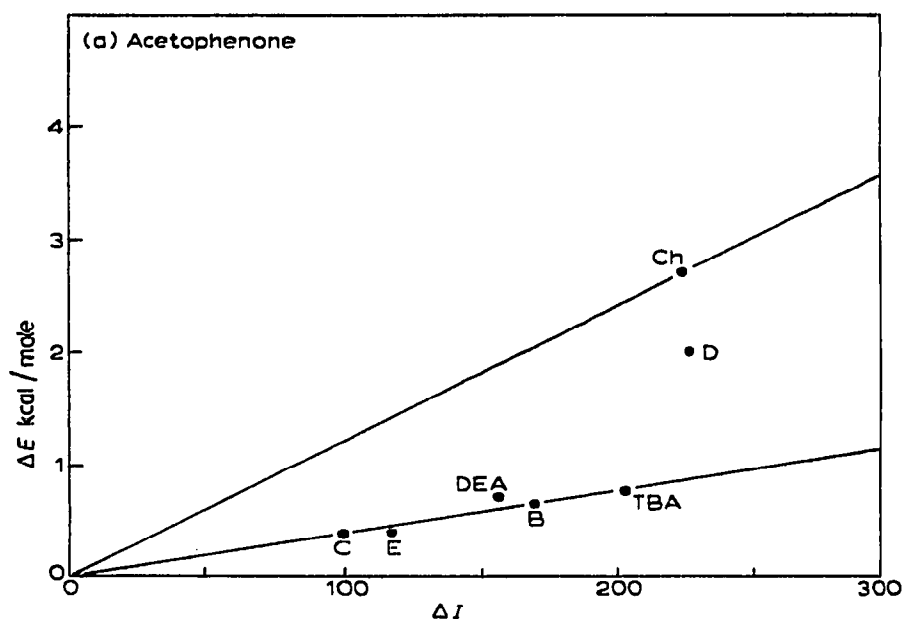
DISCUSSION

Table II lists the energy changes associated with the blue shifts together with retention indices and index increments for each solute-solvent system examined. Fig. 1 shows the relationship between energy of interaction and index increment for each stationary phase and a linear relationship is apparent in these graphs. It was unfortunate that the blue shift could not be measured for the acetophenone-alcohol and N-nitrosomethylaniline-alcohol systems as this necessitated basing the hydrogen bonding curves on only two points, the origin and the co-ordinates for chloroform in each case. The justification for this, however, is seen upon examination of the benzophenone, Fig. 1 (b) and benzil, Fig. 1 (c) systems where linear relationships are established for chloroform, ethyl and methyl alcohols.

The lower curve, in each case, is constructed from data on non-hydrogen

bonding compounds, ether, carbon tetrachloride, and can be seen to have a slope of 0.5×10^{-2} kcal.mole $^{-1}$ for benzophenone, benzil and N-nitrosomethylaniline, and 0.4×10^{-2} kcal.mole $^{-1}$ for acetophenone. This curve then, represents the London or dispersion forces of attraction between solute and solvent, describing how the retention index increment increases as dispersion force energy increases.

The upper curves in Fig. 1, particularly those in Figs. 1 (b) and 1 (c) which are each constructed through four points describe the increase in retention index increment due to total solute-solvent energy of interaction, this curve including contributions from induction, orientation and dispersion forces. However, as benzene is found on the lower curve in all cases, it must be concluded that the induction force resulting from the permanent dipole of the carbonyl or nitroso compound and the



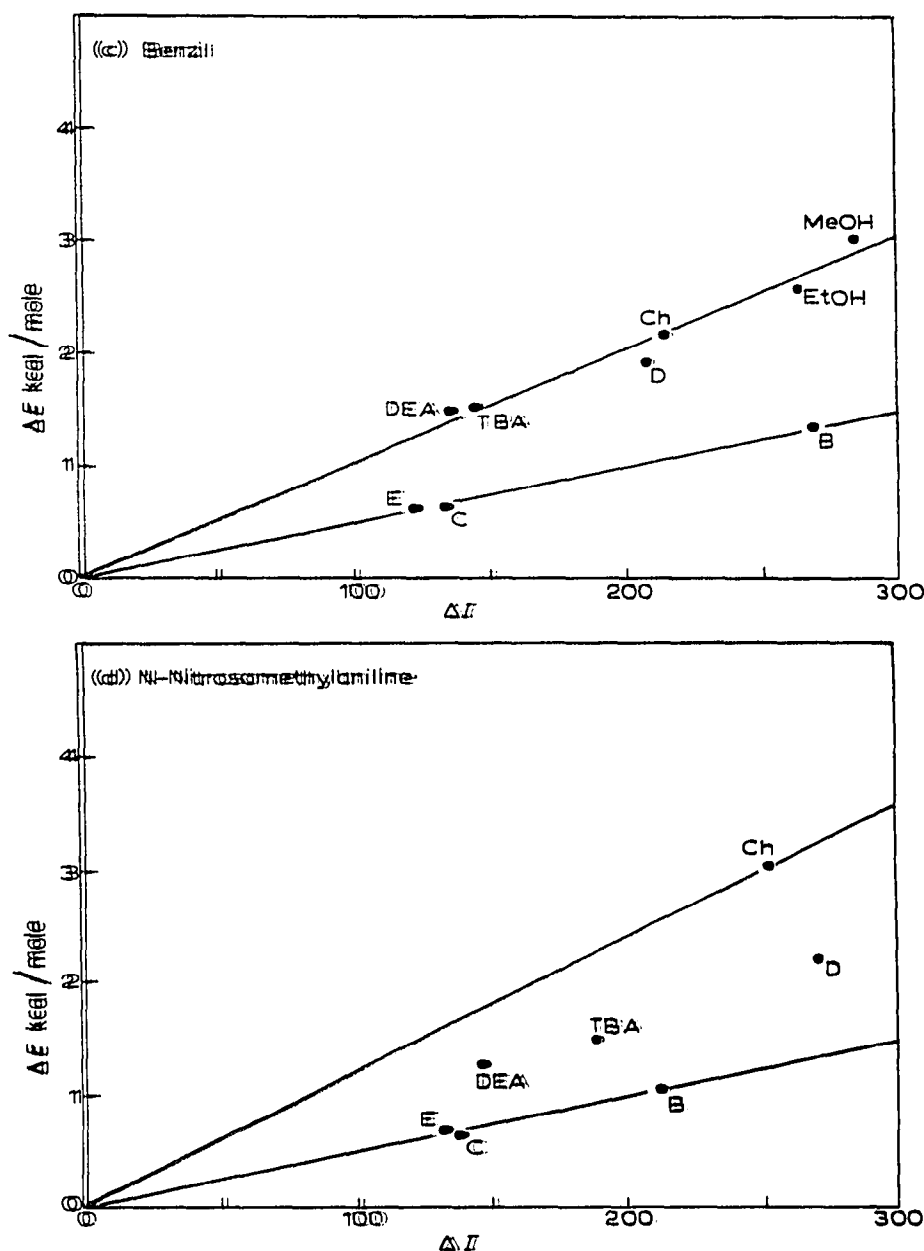


Fig. 11. Relationship between gas chromatographic retention index increment and energy associated with spectroscopic shift of $\pi \rightarrow \pi^*$ band.

induced dipole in benzene is either very small or that the lower curve in fact represents the sum of induction and dispersion forces. The difference between the two curves on the energy scale at a particular value of ΔI should then represent the orientation forces acting in the system which, in the case of the compounds studied, should amount to hydrogen bonding. As a test of this, consider the benzophenone-ethyl alcohol system. At ΔI of 260, the total energy of interaction is $3.56 \text{ kcal.mole}^{-1}$ whilst the electrostatic energy (dispersion, induction) is found, from the lower curve, to be $1.31 \text{ kcal.mole}^{-1}$. The difference gives a hydrogen bonding energy of $2.25 \text{ kcal.mole}^{-1}$ which may be compared with BREALEY AND KASHA'S¹² value of $2.6 \text{ kcal.mole}^{-1}$ derived from UV data by using a "corrected blue shift", and the more

TABLE II
UV SPECTROSCOPIC AND GAS-LIQUID CHROMATOGRAPHIC DATA

Solvent	Key to Fig. 1	Acetophenone		Benzophenone		Benzil		N-Nitrosomethyl- aniline		Squalane						
		ΔE (kcal/mole)	GLC I	ΔE (kcal/mole)	GLC I	ΔE (kcal/mole)	GLC I	ΔE (kcal/mole)	GLC I	ΔE (kcal/mole)	GLC I					
Benzene	B	0.68	804	170	0.88	812	175	1.39	824	270	1.03	851	214	637	554	1.06
Diethyl ether	E	0.42	592	118	0.61	588	114	0.67	587	123	0.70	609	135	474	464	0.20
Dichloromethane	D	2.00	707	230	2.10	705	228	1.98	697	209	2.23	750	273	477	488	-0.22
Chloroform	Ch	2.75	802	226	3.07	798	222	2.20	796	217	3.05	832	256	576	579	-0.06
Carbon tetrachloride	C	0.40	747	100	0.61	707	120	0.67	784	133	0.68	784	137	647	651	-0.08
Diethylamine	DEA	0.72	702	156	0.68	681	135	1.55	677	138	1.25	693	147	546	539	0.14
<i>tert.</i> -Butylamine	TBA	0.73	687	203	0.80	641	157	1.58	626	146	1.50	673	189	484	480	0.08
Ethyl alcohol	EtOH	^a	738	273	3.56	726	261	2.00	673	265	^a	754	289	465	468	1.14
Methyl alcohol	MeOH	^a	688	285	4.05	697	294	3.05	626	288	^a	698	295	403	338	1.30

^a It was not possible to measure the shift as the $n \rightarrow \pi^*$ band was submerged under the main benzeneoid band.

reliable IR value of $2.2 \text{ kcal}\cdot\text{mole}^{-1}$. Index increments for benzene are of interest in that the values for acetophenone and benzophenone are 170 and 175, respectively whilst a much higher value of 270 is obtained for the benzil-benzene system. This would seem to indicate a steric effect involving orientation of two *ortho* hydrogens of the benzene ring towards the two donor oxygens of the 1,2-diketone. This would explain the increased ΔI in terms of spatial geometry only if benzil was a planar molecule. JAFFÉ AND ORCHIN¹⁷ however, have pointed out that each carbonyl group is strongly conjugated to and coplanar with its phenyl group; with the minimum conjugation between the two carbonyls, evidence suggests that the two groups are twisted with respect to each other to the extent of 90° , benzil having a skew structure. If this is so, the high value of ΔI for the benzil-benzene system cannot be explained on steric grounds. An intermediate value of 214 for ΔI is found in the N-nitrosomethylaniline-benzene system. Of the nine solvents examined it is found that the largest increments occur on N-nitrosomethylaniline for six of these; benzene is anomalous with its high incremental value on benzil, the two amines having their highest increments on acetophenone. In the cases of the amines, the effect is probably steric, the small methyl group of acetophenone allowing closer approach of the N-H active hydrogen to the donor oxygen. BAYER¹⁸ has described gas chromatographic separations of trimethylamine and dimethylamine on a polyethylene oxide stationary phase and attributes these to hydrogen bonding by the secondary amine to the polyethylene oxide acceptor. No evidence of hydrogen bonding was found here for amines with acetophenone or benzophenone although this would be considered likely. On the benzil stationary phase however, the two amines are found to lie on the upper (hydrogen bonding) curve Fig. 1 (c) whilst on N-nitrosomethylaniline they occupy an intermediate position. On this phase, Fig. 1 (d), the two amines and dichloromethane lie on a straight line through the origin, a line with a slope of $0.83 \times 10^{-2} \text{ kcal}\cdot\text{mole}^{-1}$. It may be suggested that this is the upper hydrogen bonding curve with the chloroform co-ordinates in error, so experimental data for chloroform were checked and the results agreed with those previously obtained. However, the position of the upper curve in the N-nitrosomethylaniline system must be open to question until further experimental evidence is available.

Accepting the upper curves for acetophenone and N-nitrosomethylaniline as presented, it is possible to calculate the hydrogen bonding energies associated with the two compounds in methyl and ethyl alcohol. The values for acetophenone are 2.03 and 1.97 and for N-nitrosomethylaniline are 2.32 and 2.29 $\text{kcal}\cdot\text{mole}^{-1}$ for methyl alcohol and ethyl alcohol, respectively. In addition, from the total energies at the index increments of the alcohols it is possible to determine the frequencies of the $n \rightarrow \pi^*$ maxima although these values are not determinable spectroscopically due to submerging of the band. By extrapolation of the curves these band maxima are found to be: acetophenone-methyl alcohol $32,358 \text{ cm}^{-1}$, acetophenone-ethyl alcohol $32,327 \text{ cm}^{-1}$, N-nitrosomethylaniline-methyl alcohol $27,780 \text{ cm}^{-1}$, and N-nitrosomethylaniline-ethyl alcohol $27,750 \text{ cm}^{-1}$. Table III shows the hydrogen bonding energies of the four donors with the hydrogen bonding solvents measured. The calculated value for total energy of interaction between N-nitrosomethylaniline-ethyl alcohol is found to be $3.42 \text{ kcal}\cdot\text{mole}^{-1}$. This figure may be compared with a value of $3.44 \text{ kcal}\cdot\text{mole}^{-1}$ for the N-nitrosodimethylamine-ethyl alcohol system derived from spectroscopic data¹⁹.

TABLE III

(CALCULATED HYDROGEN BONDING ENERGIES FOR OXYGEN DONOR-HYDROGEN BONDING SOLVENT SYSTEMS)

Solvent	<i>H</i> -bond energy (kcal·mole ⁻¹)			
	Acetophenone	Benzophenone	Benzil	<i>N</i> -Nitrosomethylaniline
Chloroform	1.85	1.96	1.10	1.78
Diethylamine	—	—	0.82	0.50
<i>tert.</i> -Butylamine	—	—	0.83	0.57
Ethyl alcohol	1.97 ^a	2.25	1.28	2.29 ^a
Methyl alcohol	2.03 ^a	2.59	1.63	2.32 ^a

^a Estimated values.

The results obtained for aliphatic chloro hydrocarbons present a further problem. Whilst the mon hydrogen bonding carbon tetrachloride behaves ideally and, where stationary phase-alcohol spectra could be interpreted, chloroform was found to lie on the upper curve, dichloromethane takes up an intermediate position for all phases, only approaching the hydrogen bonding curve for benzil. It must therefore be assumed that some factor not apparent from spectroscopic evidence is causing dichloromethane to be retained on the column for a longer period than can be explained. Studies on an extensive range of haloparaffins are necessary before this behaviour may be interpreted. From the differences between upper and lower curves the following values of the hydrogen bonding energy for chloroform are obtained, acetophenone 1.85, benzophenone 1.96, benzil 1.10 and *N*-nitrosomethylaniline 1.78 kcal·mole⁻¹. Again, if benzil has the skew structure suggested by JAFFÉ AND ORCHIN¹⁷ it is difficult to explain the low value obtained; a value approaching the 1.95 kcal·mole⁻¹ for benzophenone would be expected. If benzil were planar however, steric hindrance could to some extent account for the low value obtained. The final column in Table II shows the variation of retention index with temperature for the nine solvents on the squalane column and it can be seen that this temperature coefficient could be the basis for a broad classification. Haloparaffins give a negative slope, amines and ethers a small positive slope and alcohols and aromatic hydrocarbons a large positive slope.

Some attempt has been made here to quantify the very complex solute-solvent interactions in gas-liquid chromatography. Obviously a large number of experimental observations are required on relatively simple hydrogen bonding systems in order to advance the underlying theory further.

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