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SELECTIVITY OF STATIONARY PHASES FOR THE RESOLUTION OF SOME SIMPLE SUBSTANCES

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SUMMARY

The relative molar heats and entropies of solution for methylbenzenes, chlorotoluenes, chlorobenzenes and chloroxylenes have been determined using the relative retentions on Apiezon L, poly(ethyleneglycoladipate), poly(phenyl ether) and methylphenylsilicone; the corresponding values for C₅-C₆ olefins were calculated on pentadecane and dinitriloadipate. It was shown that the semi-empirical theory of selectivity of the stationary phases being applied to such systems permits one to obtain reasonable results, within the limit of experimental error. The relative molar heats of solution give information about the number and nature of the substituents in the benzene ring. The difference between the relative molar heats of solution in polar and non-polar stationary phases is proposed as an analytical parameter for identification that is sensitive to the polarity of the solute. It was shown that the orientation forces in a polar stationary phase do not affect the selectivity for methyl and chlorobenzenes strongly. A "hyperconjugation" effect is discussed for the solutes under study in non-polar stationary phases and some semi-empirical equations are derived for calculating the relative molar heats of solution of methylbenzenes and olefins using this effect.

The calculated values of the relative entropies of solution permit one to estimate the positions of substituents in the benzene ring. The possibility of calculating the relative molar entropy of solution of light olefins is discussed. Some semi-empirical equations are derived for calculating the enthalpic and entropic selectivities of non-polar stationary phases.

INTRODUCTION

One of the most important problems in gas-liquid chromatography (GLC) is to establish a method for the prediction of the selectivity of stationary phases. Although many papers (for example, refs 1-6) have dealt with the problem, its theoretical solution has not been found because of difficulties encountered in the development of the general theory of dilute solutions of non-electrolytes. Therefore, a useful method of solving the problem is to develop semi-empirical theories for the predic-

tion of thermodynamic functions of solutions, which enable one to consider the selectivity on a physico-chemical basis. The total selectivity of the stationary phase (relative retention) is calculated by combining the enthalpic and entropic selectivities; two independent thermodynamic parameters of the selectivity are also a sufficient basis for identification.

The aim of this paper is to prove that the thermodynamical semi-empirical theory of the selectivity of stationary phases^{7,8} is applicable to some simple substances and to discuss the possibilities of identifying these substances by using retention data.

Let us call "simple" molecules those which are derived from benzene by replacing hydrogen atoms with chlorine or methyl groups and by replacing single C-C bonds in alkanes with double bonds. Methylbenzenes, chlorobenzenes, chlorotoluenes, chlororotoluenes, chloroxylenes and C₅-C₆ olefins on non-polar (pentadecane, Apiezon L), moderately polar [poly(phenylsilicone)PPMS-4] and polar [poly(ethylene glycol adipate), PEGA, and dinitriloadipate] stationary phases were studied.

The experiments were carried out using Chrom-2, Chrom-31 and Varian Model 1860 gas chromatographs with flame-ionization detectors. The length of the column varied from 0.8 to 1.6 m and the I.D. from 3 to 4 mm. Chromosorb G was coated with 2-4% of Apiezon L, PPMS-4 or PEGA. The solid support Inz-500 was coated with 15% of pentadecane or dinitriloadipate. The amount of each sample component was not greater than 0.01 mg. The relative retention data were measured at at least four different temperatures in the range 25-220°. The relationships between the logarithm of the relative retention and 1/T were extrapolated to a standard temperatures (50° for olefins, 100° for methylbenzenes and 150° for chloro-substituted solutes). The standard deviations of the relative retention were found to be 0.2-0.3%.

The effect of the interphase adsorption on the relative retention was investigated for dichlorobenzenes on Apiezon L. When the amount of the stationary phase was varied from 0.5 to 4%, the relative retentions of these solutes remained constant, within experimental errors. These results are in good agreement with the published data⁹.

The relative molar heats and entropies of solution were calculated by using the slope of the logarithm of the relative retention as a function of 1/T and relative retentions at standard temperature^{10,11}. The mean standard deviations of the calculated molar relative enthalpies and entropies of solution were 0.07 kcal/mole and 0.15 e.u., respectively.

ENTHALPIC SELECTIVITY FOR AROMATIC SOLUTES

The relative molar heat of solution (enthalpic selectivity) is calculated using the following equations⁷:

$$\Delta H_s^\circ = \Delta H_L^\circ + \Delta H_h^\circ \quad (1)$$

$$\Delta H_L^\circ = i \sum_{n_0} K_{n_0} D_{n_0} \quad (2)$$

where

ΔH_L° = relative energy of the intermolecular interaction;

ΔH_h° = relative energy of hole formation;

- K_{n_0} = coefficient of intramolecular shielding;
 D_{n_0} = dispersion interaction index;
 n_0 = atomic group of the solute molecule;
 i = normalization coefficient.

Let us calculate the molar heat of solution for benzene in Apiezon L using eqns. 1 and 2. The benzene molecule can be divided into six CH groups, each of which interacts with the environment in the plane of the benzene ring (A) and in the plane perpendicular to it (B). The Van der Waals radii of a CH group in planes A and B are 2.0 and 1.85 Å, respectively¹². K_{n_0} for a CH group in benzene is 0.45. Then, $K_{n_0}D_{n_0}$ values⁷ for a CH group in planes A and B are 2.19 and 2.79, respectively. Every CH group has one contact point with the environment in plane A and two contact points in plane B. Therefore, $K_{n_0}D_{n_0} = (2.19 \cdot 0.33) + (2.79 \cdot 0.67) = 2.59$.

These values were calculated for all of the solutes studied (Table I). As was shown earlier¹³, the difference between the calculated (ΔH_L°) and experimental (ΔH_{se}°) molar heats of solution, \bar{F} , is related to the steric hindrance. In order to estimate an effect of substitution in the benzene ring on the molar heat of solution, the values $\delta\bar{F} = \bar{F}_x - \bar{F}_{bz}$ are used, where bz refers to benzene (Table I).

The relationship between the $\delta\bar{F}$ values and the number of the vicinal methyl groups in methylbenzene molecules is expressed as follows:

$$\delta\bar{F}_c = 0.25 - 0.01n \quad (3)$$

where n is the number of substituted groups in the benzene ring. The corresponding relationships for chlorobenzenes, chlorotoluenes and chloroxylenes, respectively, are

$$\delta\bar{F}_c = 0.67n \quad (4)$$

$$\delta\bar{F}_c = 0.51n + 0.65 \quad (5)$$

$$\delta\bar{F}_c = 0.49n + 1.05 \quad (6)$$

The mean standard deviations of the $\delta\bar{F}_c - \delta\bar{F}$ values for methylbenzenes, chlorobenzenes, chlorotoluenes and chloroxylenes are 0.07, 0.06, 0.2 and 0.1 kcal/mole, respectively. Hence the calculated $\delta\bar{F}_c$ values are the same as those found experimentally, within experimental error.

Let us discuss the effect of the number of substituents in the benzene ring on the value of $\delta\bar{F}$. All of the $\delta\bar{F}$ values for methylbenzenes are virtually identical, because the heat of hole formation is compensated for by an increase in the energy of hyperconjugation¹³. As a consequence of hyperconjugation, an electron cloud passes partially from the methyl group to the benzene ring and the Van der Waals radius of this methyl group is decreased; in accordance with the London equation the latter leads to an increase in the energy of intermolecular interaction.

The Van der Waals radius of the benzene molecule is increased when a hydrogen atom is replaced with a methyl group or chlorine atom; then the energy of hole formation is increased by transition from benzene to methylbenzenes. As shown earlier¹³, the difference between the energies of hole formation of toluene and benzene is about 0.6 kcal/mole; if the $\delta\bar{F}_c$ value for all methylbenzenes is virtually constant, the energy of "hyperconjugation" is about -0.6 kcal/mole per methylene group. The

TABLE I

MOLAR HEATS OF SOLUTION (kcal/mole) OF THE SUBSTANCES UNDER STUDY IN APIEZON I

Solute	D_i	$-i$	$-\Delta H_L^\circ$	$-\Delta H_{sc}^\circ$	F	δF
Benzene	15.5	0.454	7.04	6.34	0.70	0
Toluene	18.45	0.448	8.28	7.34	0.94	0.24
<i>o</i> -Xylene	21.3	0.447	9.52	8.65	0.87	0.17
<i>m</i> -Xylene	21.3	0.447	9.52	8.51	1.01	0.31
<i>p</i> -Xylene	21.3	0.447	9.52	8.51	1.01	0.31
1,2,3-Trimethylbenzene	24.2	0.447	10.85	9.90	0.95	0.25
1,2,4-Trimethylbenzene	24.2	0.447	10.85	9.63	1.22	0.52
1,3,5-Trimethylbenzene	24.2	0.447	10.85	9.66	1.19	0.49
1,2,4,5-Tetramethylbenzene	27.1	0.447	12.15	10.88	1.27	0.57
1,2,3,5-Tetramethylbenzene	27.1	0.447	12.15	11.00	1.15	0.45
Pentamethylbenzene	30.0	0.447	13.4	12.42	1.02	0.32
Hexamethylbenzene	32.9	0.447	14.75	13.95	0.80	0.10
Chlorobenzene	20.6	0.456	9.40	8.10	1.30	0.60
<i>o</i> -Dichlorobenzene	24.8	0.462	11.6	9.35	2.15	1.45
<i>p</i> -Dichlorobenzene	24.8	0.462	11.6	9.30	2.20	1.50
<i>m</i> -Dichlorobenzene	24.8	0.462	11.6	9.30	2.20	1.50
1,2,3-Trichlorobenzene	29.0	0.472	13.7	10.95	2.75	2.05
1,2,4-Trichlorobenzene	29.0	0.472	13.7	10.85	2.85	2.15
1,3,5-Trichlorobenzene	29.0	0.472	13.7	10.85	2.85	2.15
1,2,3,5-Tetrachlorobenzene	33.9	0.472	15.7	12.1	3.6	2.9
1,2,4,5-Tetrachlorobenzene	33.9	0.472	15.7	12.1	3.6	2.9
1,2,3,4-Tetrachlorobenzene	33.9	0.472	15.7	12.35	3.35	2.65
Pentachlorobenzene	37.4	0.472	17.65	13.55	4.1	3.4
Hexachlorobenzene	41.6	0.472	19.65	14.9	4.75	4.05
<i>o</i> -Chlorotoluene	22.7	0.46	10.45	8.85	1.6	0.9
<i>m</i> -Chlorotoluene	22.7	0.46	10.45	8.85	1.6	0.9
<i>p</i> -Chlorotoluene	22.7	0.46	10.45	8.85	1.6	0.9
2,6-Dichlorotoluene	26.9	0.465	12.5	10.45	2.05	1.35
2,5-Dichlorotoluene	26.9	0.465	12.5	10.45	2.05	1.35
2,4-Dichlorotoluene	26.9	0.465	12.5	10.45	2.05	1.35
2,4,6-Trichlorotoluene	31.1	0.47	14.65	11.75	2.85	2.15
2,4,5-Trichlorotoluene	31.1	0.47	14.65	11.8	2.8	2.1
2,3,5-Trichlorotoluene	31.1	0.47	14.65	11.8	2.8	2.1
2,3,6-Trichlorotoluene	31.1	0.47	14.65	12.05	2.55	1.85
2,3,4-Trichlorotoluene	31.1	0.47	14.65	12.2	2.4	1.7
2,3,5,6-Tetrachlorotoluene	35.3	0.47	16.6	13.2	3.4	2.7
2,3,4,5-Tetrachlorotoluene	35.3	0.47	16.6	13.35	3.25	2.55
Pentachlorotoluene	39.5	0.47	18.55	14.8	3.75	3.05
<i>o</i> -Chloro- <i>p</i> -xylene	25.5	0.46	11.75	9.85	1.9	1.2
2,5-Dichloro- <i>p</i> -xylene	29.7	0.46	13.7	11.4	2.3	1.6
2,3-Dichloro- <i>p</i> -xylene	29.7	0.46	13.7	11.55	2.15	1.45
2,3,5-Trichloro- <i>p</i> -xylene	33.9	0.46	15.75	12.85	2.9	2.2

effect of hyperconjugation does not occur for chlorobenzenes (see eqn. 6); the δF_c values are positive and proportional to n .

Let us compare the \bar{F} values of isomers. Let $f = \delta \bar{F}_c - \delta F_e$ (δF_e is the experimental value for the given isomer and $\delta \bar{F}_c$ is the calculated value for vicinal isomer). The random position of substituents increases the effective volume of the molecule compared with the vicinal isomer, and therefore the f values for vicinal isomers are

TABLE II

VALUES OF f (kcal/mole) FOR THE SOLUTES UNDER STUDY IN APIEZON L

Solute	f	Solute	f
<i>m</i> -Xylene	0.09	<i>m</i> -Chlorotoluene	0
<i>p</i> -Xylene	0.09	<i>p</i> -Chlorotoluene	0
1,2,4-Trimethylbenzene	0.30	2,6-Dichlorotoluene	-0.16
1,3,5-Trimethylbenzene	0.27	2,5-Dichlorotoluene	-0.16
1,2,4,5-Tetramethylbenzene	0.36	2,4-Dichlorotoluene	-0.16
1,2,3,5-Tetramethylbenzene	0.24	2,4,6-Trichlorotoluene	0.15
<i>m</i> -Dichlorobenzene	0.18	2,4,5-Trichlorotoluene	0.05
<i>p</i> -Dichlorobenzene	0.18	2,3,5-Trichlorotoluene	0.05
1,2,4-Trichlorobenzene	0.17	2,3,6-Trichlorotoluene	-0.17
1,3,5-Trichlorobenzene	0.17	2,3,5,6-Tetrachlorotoluene	0.16
1,2,3,5-Tetrachlorobenzene	0.25	2,3-Dichloro- <i>p</i> -xylene	-0.10
1,2,4,5-Tetrachlorobenzene	0.25		

smaller than for non-vicinal isomers. Hence the differences in f values show the vicinal or non-vicinal position of homogeneous substituents (not, for example, for chlorotoluenes). The f values for the solutes studied are given in Table II.

In going from a non-polar to a polar stationary phase, some other factors in the enthalpic selectivity appear, such as the orientation interaction; the energy of hole formation and the interphase adsorption also change. A complete account of all of the new factors is virtually impossible and only the application of a comparative technique permits one to overcome some of the difficulties that arise.

The Van der Waals radii of a methyl group and a chlorine atom are actually very close (2.0 and 1.8 Å, respectively), and therefore the Van der Waals volumes of the homomorphous chlorobenzene, chlorotoluene and methylbenzene molecules may be considered to be identical; hence, the energy of hole formation for these homomorphous molecules is the same. We denote as the homomorphous those molecules which have the same number and positions of the substituents. Let us denote a variation in the relative heat of solution in passing from a non-polar to a polar stationary phase as δH_s° , and $\delta \bar{H}_s^\circ = \delta H_{sx}^\circ - \delta H_{sh}^\circ$ (x is the solute under study, and h is the homomorphous methylbenzene):

$$\delta \bar{H}_s^\circ = \beta n_{Cl} + \Delta O \quad (7)$$

where n_{Cl} = number of chlorine atoms in the molecule;

β = coefficient expressing a deviation of the dispersion energy;

ΔO = difference in the orientation energy.

The dispersion interaction energy for a chlorine atom is greater than that for a methyl group⁷ and therefore β must be negative; the dipole moment of Ar-Cl is also much greater than for Ar-CH₃ (1.5 and 0.4 D, respectively) and therefore the ΔO value also must be negative.

The results in Table III show that $\delta \bar{H}_s^\circ$ is positive for chlorobenzene and is close to zero for all other vicinal chlorobenzenes. This result indicates a very weak orientation interaction for the systems under study. Every dipole group Ar-Cl in the vicinal chlorobenzenes is shielded, which decreases the orientation interaction energy; for non-vicinal isomers, this shielding is lower and therefore the $\delta \bar{H}_s^\circ$ values for non-

TABLE III
RELATIVE MOLAR HEATS OF SOLUTION (kcal/mole) IN POLAR STATIONARY PHASES

Solute	Stationary phase				
	PEGA		PPE		PPMS-4
	$-\Delta H_s^\circ$	δH_s° *	$-\Delta H_s^\circ$	δH_s°	$-\Delta H_s^\circ$
Toluene	0.84	0.16	0.96	0.04	—
<i>o</i> -Xylene	2.05	0.16	2.11	0.20	—
<i>m</i> -Xylene	1.82	0.35	1.98	0.19	—
<i>p</i> -Xylene	1.76	0.41	1.79	0.38	—
1,2,3-Trimethylbenzene	3.17	0.39	3.48	0.08	—
1,2,4-Trimethylbenzene	2.87	0.42	3.01	0.28	—
1,3,5-Trimethylbenzene	2.77	0.55	2.96	0.36	—
1,2,4,5-Tetramethylbenzene	3.93	0.61	4.01	0.53	—
1,2,3,5-Tetramethylbenzene	3.96	0.70	4.12	0.54	—
Pentamethylbenzene	5.18	0.88	5.41	0.65	—
Hexamethylbenzene	6.58	1.03	6.61	1.00	—
Chlorobenzene	1.30	0.35	—	—	1.61
<i>o</i> -Dichlorobenzene	2.90	-0.06	—	—	3.00
<i>p</i> -Dichlorobenzene	2.70	-0.16	—	—	2.90
<i>m</i> -Dichlorobenzene	2.55	0.05	—	—	2.90
1,2,3-Trichlorobenzene	4.30	-0.09	—	—	4.50
1,2,4-Trichlorobenzene	4.15	-0.07	—	—	4.30
1,3,5-Trichlorobenzene	3.50	-0.35	—	—	4.00
1,2,3,5-Tetrachlorobenzene	5.10	-0.05	—	—	5.50
1,2,4,5-Tetrachlorobenzene	5.15	-0.01	—	—	5.50
1,2,3,4-Tetrachlorobenzene	5.55	—	—	—	5.85
Pentachlorobenzene	6.35	-0.03	—	—	6.84
Hexachlorobenzene	7.55	-0.03	—	—	8.20
<i>o</i> -Chlorotoluene	2.10	0.24	—	—	2.35
<i>m</i> -Chlorotoluene	2.30	-0.15	—	—	2.40
<i>p</i> -Chlorotoluene	2.30	-0.21	—	—	2.40
2,6-Dichlorotoluene	3.50	0.30	—	—	3.80
2,5-Dichlorotoluene	3.60	0.08	—	—	3.80
2,4-Dichlorotoluene	3.50	0.18	—	—	3.70
2,4,6-Trichlorotoluene	4.30	0.40	—	—	4.80
2,4,5-Trichlorotoluene	4.75	0.09	—	—	5.25
2,3,5-Trichlorotoluene	4.80	-0.05	—	—	5.20
2,3,6-Trichlorotoluene	4.80	—	—	—	5.20
2,3,4-Trichlorotoluene	5.20	—	—	—	5.35
2,3,5,6-Tetrachlorotoluene	5.85	0.12	—	—	6.50
2,3,4,5-Tetrachlorotoluene	6.40	-0.28	—	—	6.85
Pentachlorptoluene	7.10	0.30	—	—	8.00
<i>o</i> -Chloro- <i>p</i> -xylene	2.90	0.18	—	—	3.40
2,5-Dichloro- <i>p</i> -xylene	4.20	0.24	—	—	4.80
2,3-Dichloro- <i>p</i> -xylene	4.35	—	—	—	5.00
2,3,5-Trichloro- <i>p</i> -xylene	5.40	0.22	—	—	6.20

* These values for chloro-substituted solutes are actually the $\delta \bar{H}_s^\circ$ values.

vicinal isomers are more negative than those for vicinal isomers. This can clearly be seen for di- and trichlorobenzenes; the differences for tetrachlorobenzenes are negligible.

Chlorobenzenes have only homogeneous dipoles, while chlorotoluenes and

chloroxylenes have two different types of dipoles. For chlorobenzenes, shielding strongly affects on the δH_s° values: δH_s° for *p*-chlorotoluene is 0.5 kcal/mole lower than that for *o*-chlorotoluene. This difference is much greater than for dichlorobenzene isomers. With a non-polar stationary phase, shielding of the methyl group by chlorine atoms in chlorotoluenes affects the δH_s° values of the isomers. For example, in passing from 2,3,4,5- to 2,3,5,6-tetrachlorotoluene, the orientation interaction energy is reduced by 0.4 kcal/mole.

One of the most important analytical problems in GLC is the resolution of mixtures containing isomers; the identification of these isomers is also a difficult problem. As the relative molar enthalpy of solution is a parameter for identification, it is important to investigate the relationship between the position of a substituent in the benzene ring and the differences in the relative molar heats of solution in going from a non-polar to a polar stationary phase. Such relationships are shown in Fig. 1. As a rule they can be expressed in terms of linear plots. The difference between the relative molar heats of solution in a polar (PEGA) and a non-polar (Apiezon L) stationary phase (δH_s°) is described by the equation

$$\delta H_s^\circ = \bar{c} + 0.24n \quad (8)$$

The constant \bar{c} is -0.30 , -0.35 , -0.08 and -0.08 kcal/mole for methylbenzenes, chlorobenzenes, chloroxylenes and chlorotoluenes, respectively. Eqn. 8 is valid for solutes with $n \geq 2$. All solutes in eqn. 8 are vicinal isomers.

Let us discuss eqn. 8. The δH_s° value is the difference in the relative molar heats of solution for homomorphous molecules, *i.e.*, in this instance the different energies of hole formation in polar and non-polar stationary phases are not taken into account. δH_s° includes the latter difference. A polar stationary phase is a more rigid structure than a non-polar one and therefore the energy of hole formation for the polar stationary phase must be higher than that for a non-polar one. The energy of hole formation

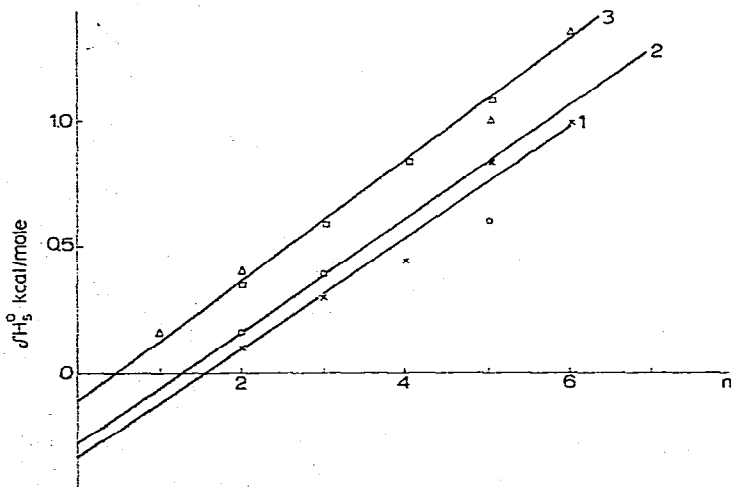


Fig. 1. Relationships between δH_s° values and the number of substituents in the benzene ring for vicinal isomers (the stationary phases are PEGA and Apiezon L). 1, Chlorobenzenes; 2, methylbenzenes; 3, chlorotoluenes (Δ) and chloroxylenes (\square).

is proportional to the Van der Waals volume of a molecule and hence to the number of substituents in the benzene ring. All substituent groups in the solute molecules under study have the same Van der Waals volume, which is why the slopes in Fig. 1 are identical.

The \bar{c} value in eqn. 8 reflects a variation in the energy of interaction in going from non-polar to polar stationary phases. The more positive the \bar{c} value, the weaker is the interaction energy for homologous series of vicinal isomers. The dipole moments of chlorotoluene molecules are much higher than those of chloro- and methylbenzenes, and therefore the orientation interaction energy for chlorotoluenes in a polar stationary phase are the highest. However, Fig. 1 shows that a line for chlorotoluenes is located higher than those for methyl- and chlorobenzenes. This is additional evidence that the orientation interaction energy has a small influence on δH_s° . It is interesting that the lines for some homologous series in Fig. 1 are clearly separated; thus, the position of the experimentally found point for an unknown solute shows the number and nature of the substituent groups. The data in Fig. 1 enable one to establish the the above-mentioned parameters for the unknown molecules using two independent values.

The energy of hole formation is very sensitive to the arrangement of substituents in the benzene ring. For example, the δH_s° values for the most difficult to resolved isomers of xylenes and dichlorobenzenes are different, which is useful as a basis for identification. However, a variation in the polarity of a stationary phase does not result in a difference in enthalpic selectivity for *p*- and *m*-chlorotoluenes. The 1,3,5-isomer for trisubstituted homogeneous compounds has the maximal value of δH_s° .

The difference in the relative molar heats of solution in polar and non-polar stationary phases in a sensitive parameter for the identification of simple aromatic molecules. By comparing these parameters, it is possible to draw conclusions about the number of substituents in the benzene ring, their homogeneity and the nature of partially and fully shielded methyl groups in chlorotoluenes.

The phenylsilicone stationary phase PPMS-4 is a high-temperature liquid of intermediate polarity. Its enthalpic selectivity towards isomeric chlorobenzenes is intermediate between the values for non-polar and polar stationary phases (Table III).

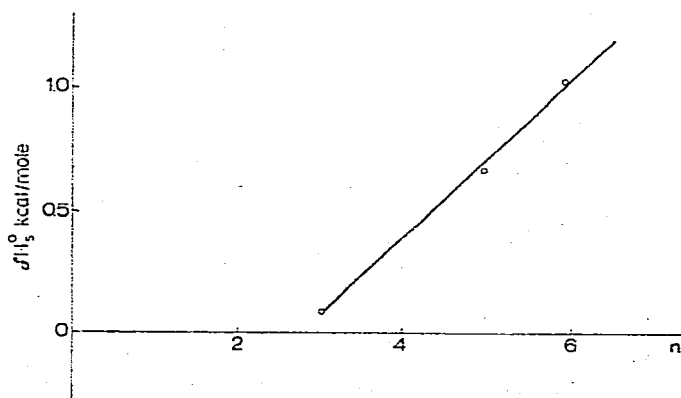


Fig. 2. Relationship between δH_s° values and the number of methyl groups in the vicinal methylbenzene molecule. The stationary phases are PPE and Apiezon L.

Hence the enthalpic selectivity of an intermediate polar stationary phase does not make a new contribution to the selectivity; such a selectivity can be obtained by using an appropriate mixture of polar and non-polar stationary phases.

Poly(phenyl ether) (PPE) is a stationary phase that is selective for the resolution of geometrical isomers, *i.e.*, it has "structural" selectivity. This stationary phase has a rigid structure consisting of aromatic rings connected by ether linkages. The δH_s° values for vicinal methylbenzenes using PPE are shown in Fig. 2. It can be seen that the isomeric selectivity on PPE is different from those obtained on PEGA. For example, the δH_s° value of *o*-xylene on PPE deviates substantially from those for other isomers. The non-vicinal trimethylbenzenes have δH_s° values that are much higher than those for the vicinal isomers. Such results indicate the possibility of using a "structural" selective stationary phase for the identification of isomers with two or three substituents that are difficult to resolve.

ENTROPIC SELECTIVITY OF STATIONARY PHASES FOR BENZENE DERIVATIVES

As was shown earlier⁸, there is a relationship between the relative molar entropy of solution (ΔS_s°) and the "compensation" effect ($c\Delta H_s^\circ/T$):

$$\Delta S_s^\circ = c\Delta H_s^\circ/T + F \quad (9)$$

where

$$F = R \ln M_x/M_r + c'R \ln J_x/J_r - c'R \ln \sigma_x/\sigma_r;$$

$$R = R \ln M^\circ + c'R \ln J^\circ - c'R \ln \sigma^\circ;$$

J = moment of inertia of the solute molecule, which is equal to Mr^2 , where r is the radius of rotation;

M = molecular weight;

σ = degree of symmetry;

c' = degree of hindrance of the rotation of the molecule in the solution.

All of the derivatives under study have an internal rotation that does not change the conformation of the solute molecule, and therefore the internal rotation is not hindered in a non-polar stationary phase solution and we take into account only variations in the entropy of external rotation during condensation of the solute molecules from the gas phase into solution.

In order to calculate the moments of inertia for solute molecules, we used data on molecular geometrical structure, lengths of bonds in Ångströms and molecular weights in hydrogen units. The total moment of inertia of a particle is found as the product of the moments of inertia of the projections of the molecule on three axes of coordinates. The moment of inertia of the molecule is calculated as the sum of the moments of inertia of all atoms or atomic groups for the molecule. The rotational radius of a carbon atom in a benzene ring is 1.4 Å, for a methyl group is 2.94 Å and for a chlorine atom 3.16 Å. For all solutes, $J^\circ \gg M^\circ$, and we can therefore neglect the term $R \ln M^\circ$. To a first approximation, we also neglect the term containing the degree of symmetry. Then

$$\Delta S_s^\circ = c^\circ \Delta H_s^\circ + 4.58 c' \log J^\circ \quad (10)$$

where $c^\circ = c/T$.

Let us calculate the constants in eqn. 10 using data for very similar solutes, viz., penta- and hexamethylbenzenes, on Apiezon L at 100°. Then we can write the following two equations for hexa- and pentamethylbenzene, respectively:

$$5.27c' + 7.61c'' = 8.97 \quad (11)$$

$$4.94c' + 6.06c'' = 7.19 \quad (12)$$

Solving these equations, we found c' and c'' to be 0.0655 and 1.1336, respectively. Using eqn. 10, the relative molar entropies in Apiezon L were calculated and are listed in Table IV (ΔS_{sc}°). The error of this technique is $\delta S_s^\circ = \Delta S_{se}^\circ - \Delta S_{sc}^\circ$, ΔS_{se}° being values calculated from experimental retention data.

Taking into account that $c'' = c/T$, the coefficient c'' can be re-calculated to 150° and found to be 1.00. The c' values for chloro derivatives were calculated by solving eqn. 10 for penta- and hexachlorobenzenes. The mean value of c' for chlorobenzenes is the same as for methylbenzenes (0.0655). As can be seen from Table IV, the mean standard deviation of the calculated values of ΔS_{sc}° from the experimental values is 0.22 e.u., which is close to the errors in gas chromatographic determinations.

To obtain more precise results, let us discuss some special features of the solutes under study. Fig. 3 is a plot of δS_s° versus the number of substituents in the benzene ring for homologous series of vicinal isomers. These relationships are approximated by straight lines according to following equations for methylbenzenes, chloroxylenes, chlorotoluenes and chlorobenzenes, respectively:

$$\delta S_{sc}^\circ = 0.06 - 0.01n \quad (14)$$

$$\delta S_{sc}^\circ = 0.09 - 0.05n \quad (15)$$

$$\delta S_{sc}^\circ = 0.31 - 0.06n \quad (16)$$

$$\delta S_{sc}^\circ = 0.95 - 0.15n \quad (17)$$

where n is the number of substituents in the benzene ring.

Taking into account these four equations, the mean standard deviations of the calculated values of the molar entropy of solution are decreased for methylbenzenes, chloroxylenes, chlorotoluenes and chlorobenzenes to 0.03, 0.07, 0.05 and 0.04 e.u., respectively.

Let us consider the relative molar entropies of solution for isomeric substances. As can be seen from Table IV, vicinal isomers have the maximal ΔS_s° values. Let us estimate the positions of substituents in the benzene ring quantitatively using the term "positional entropy". Thermodynamic definitions give entropy as a function of the thermodynamic probability W , using the Boltzman constant, k :

$$S = k \ln W \quad (18)$$

Let us introduce some formal approaches. The benzene ring has six positions for bonding with substituents. The vicinal position of substituents is the more rigid, "packed" structure; such isomers have the minimal value of positional entropy.

TABLE IV
RELATIVE MOLAR ENTROPIES OF SOLUTION (e.u.) IN APIEZON L

Solute	$A = 4.58 \log J^\circ$	$c'A$	$c''\Delta H_s^\circ$	ΔS_{sc}°	ΔS_{se}°	δS_s°
Toluene	1.47	-0.10	-1.12	-1.22	-1.18	0.04
<i>p</i> -Xylene	2.36	-0.15	-2.46	-2.61	-2.75	-0.14
<i>m</i> -Xylene	2.87	-0.19	-2.46	-2.65	-2.74	-0.09
<i>o</i> -Xylene	2.87	-0.19	-2.62	-2.81	-2.77	0.04
1,3,5-Trimethylbenzene	3.24	-0.21	-3.77	-3.98	-4.27	-0.29
1,2,4-Trimethylbenzene	3.15	-0.20	-3.75	-3.95	-3.91	0.04
1,2,3-Trimethylbenzene	3.24	-0.21	-4.05	-4.26	-4.30	-0.04
1,2,4,5-Tetramethylbenzene	3.68	-0.24	-5.15	-5.39	-5.48	-0.09
1,2,3,5-Tetramethylbenzene	3.68	-0.24	-5.28	-5.52	-5.67	-0.15
Chlorobenzene	2.82	-0.18	-1.75	-1.93	-2.04	-0.11
<i>p</i> -Dichlorobenzene	3.92	-0.26	-2.94	-3.20	-2.90	0.30
<i>m</i> -Dichlorobenzene	5.14	-0.33	-2.95	-3.28	-2.90	0.38
<i>o</i> -Dichlorobenzene	5.14	-0.33	-3.00	-3.33	-2.67	0.66
1,3,5-Trichlorobenzene	6.22	-0.40	-4.50	-4.90	-5.08	-0.18
1,2,4-Trichlorobenzene	6.00	-0.39	-4.50	-4.89	-4.73	0.16
1,2,3-Trichlorobenzene	6.22	-0.40	-4.60	-5.00	-4.49	0.51
1,2,3,5-Tetrachlorobenzene	6.96	-0.45	-5.75	-6.20	-6.01	0.19
1,2,4,5-Tetrachlorobenzene	6.96	-0.45	-5.75	-6.20	-5.99	0.21
1,2,3,4-Tetrachlorobenzene	6.96	-0.45	-6.00	-6.45	-6.01	0.44
<i>o</i> -Chlorotoluene	4.28	-0.28	-2.50	-2.78	-2.58	0.20
<i>m</i> -Chlorotoluene	4.28	-0.28	-2.50	-2.78	-2.57	0.21
<i>p</i> -Chlorotoluene	3.32	-0.22	-2.50	-2.72	-2.56	0.16
2,6-Dichlorotoluene	5.55	-0.36	-4.10	-4.46	-4.52	-0.06
2,5-Dichlorotoluene	5.55	-0.36	-4.10	-4.46	-4.51	-0.05
2,4-Dichlorotoluene	5.55	-0.36	-4.10	-4.46	-4.51	-0.05
2,4,6-Trichlorotoluene	6.55	-0.43	-5.40	-5.83	-5.82	0.01
2,4,5-Trichlorotoluene	6.55	-0.43	-5.45	-5.88	-5.74	0.14
2,3,5-Trichlorotoluene	6.45	-0.43	-5.45	-5.88	-5.76	0.12
2,3,6-Trichlorotoluene	6.45	-0.43	-5.70	-6.13	-6.26	-0.13
2,3,4-Trichlorotoluene	6.55	-0.43	-5.83	-6.26	-6.27	-0.01
2,3,5,6-Tetrachlorotoluene	7.25	-0.47	-6.86	-7.33	-7.24	0.09
2,3,4,5-Tetrachlorotoluene	7.30	-0.47	-7.00	-7.47	-7.20	0.27
Pentachlorotoluene	7.90	-0.51	-8.43	-8.94	-9.13	-0.19
<i>o</i> -Chloro- <i>p</i> -xylene	4.82	-0.31	-3.50	-3.81	-3.86	-0.05
2,3-Dichloro- <i>p</i> -xylene	6.00	-0.39	-5.05	-5.44	-5.65	-0.21
2,5-Dichloro- <i>p</i> -xylene	6.00	-0.39	-5.20	-5.59	-5.62	-0.03
2,3,5-Trichloro- <i>p</i> -xylene	6.95	-0.45	-6.50	-6.95	-7.07	-0.12

Moving the substituents apart to other possible positions in the benzene ring, we obtain isomers with higher positional entropies. Let us assume that for two substituents in the *ortho*-, *meta*- and *para*-positions W is 1, 2 and 3, respectively. For 1, 2,3-trimethylbenzene, $W = 1 \times 1$ because two pairs of methyl groups in this molecule are in *ortho*-positions; for the same reason, 1,2,4- and 1,3,5-trimethylbenzenes have W equal to 1×2 and 2×2 , respectively. Therefore, the decrease in rotational entropy during solution will be proportional to the positional entropy of the isomer. This loss ($\bar{f} = \delta S_{sc}^\circ - \delta S_{se}^\circ$, δS_{sc}° being calculated for the vicinal isomer) is as follows for methylbenzenes and chlorobenzenes, respectively:

$$\bar{f} = -3.3 \log W \quad (19)$$

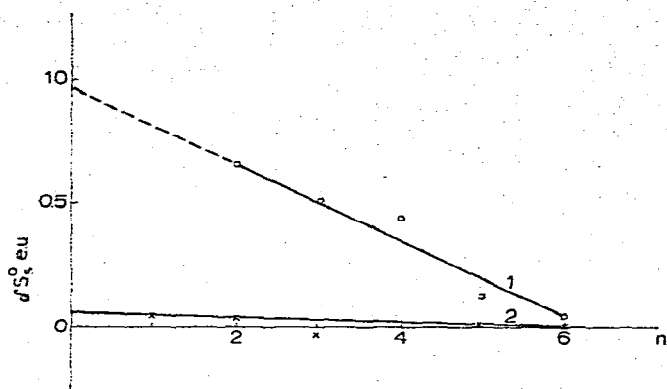


Fig. 3. Relationships between δS_s° values and the number of substituents in the benzene ring for vicinal isomers of chlorobenzenes (1) and methylbenzenes (2) in Apiezon L.

$$\bar{f} = -6.6 \log W \quad (20)$$

The mean standard deviation for calculated values of isomeric substances is 0.04 e.u. The numerical constants in the last two equations express the differences in the molecular weights of the substituents. Values of \bar{f} on Apiezon L are given in Table V.

A comparison of data for chlorotoluenes with partially (2,3-dichloro-) and fully (2,6-dichloro-) shielded methyl groups shows that the latter isomers have \bar{f} values that are 0.2 e.u. lower.

Thus, we can write the total equations for the calculation of the relative molar entropies of solution for methylbenzenes and chlorobenzenes, respectively, in Apiezon L, as

$$\Delta S_s^\circ = 1.1336 \Delta H_s^\circ + 0.0655 \cdot 4.58 \log J^\circ - 0.01n + 0.06 - 3.3 \log W \quad (21)$$

$$\Delta S_s^\circ = \Delta H_s^\circ + 0.0655 \cdot 4.58 \log J^\circ - 0.15n + 0.95 - 6.6 \log W \quad (22)$$

The relative molar entropies of solution in PEGA and PPMS-4 are listed in Table VI. The coefficients c' calculated from experimental data for PPMS-4 and

TABLE V
VALUES OF \bar{f} (e.u.) ON APIEZON L

Solute	\bar{f}	Solute	\bar{f}
<i>m</i> -Xylene	-0.13	2,6-Dichlorotoluene	-0.19
<i>p</i> -Xylene	-0.18	2,4,5-Trichlorotoluene	0.07
1,2,4-Trimethylbenzene	0.01	2,3,6-Trichlorotoluene	-0.20
1,3,5-Trimethylbenzene	-0.32	2,3,5,6-Tetrachlorotoluene	0.08
1,2,3,5-Tetramethylbenzene	-0.17	2,3,4,5-Tetrachlorotoluene	0.26
1,2,4,5-Tetramethylbenzene	-0.11	<i>m</i> -Dichlorobenzene	-0.28
<i>m</i> -Chlorotoluene	0.01	<i>p</i> -Dichlorobenzene	-0.36
<i>p</i> -Chlorotoluene	-0.04	1,2,4-Trichlorobenzene	-0.35
2,4-Dichlorotoluene	-0.18	1,3,5-Trichlorobenzene	-0.69
2,5-Dichlorotoluene	-0.18	1,2,3,5-Tetrachlorobenzene	-0.25
2,3,5-Trichlorotoluene	0.05	1,2,4,5-Tetrachlorobenzene	-0.23

PEGA are 0.096 and 0.147, respectively, which indicate the greater hindrance of rotation in these more polar stationary phases than in Apiezon L. These coefficients are proportional to the polarity of the stationary phase.

The mean standard deviations of relative molar entropies of solution calculated using the described technique in the polar stationary phases are much greater (0.8 e.u.) than for Apiezon L, which is a limitation of the method. The relationships between the δS_i° values and the number of substituents in the benzene ring for homologous series of vicinal isomers using the polar stationary phases are non-linear.

Thus, a discussion of the experimental data for simple aromatic substances has shown that it is possible to apply the semi-empirical theory of selectivity of the station-

TABLE VI

RELATIVE MOLAR ENTROPIES OF SOLUTION (e.u.) IN PEGA AND PPMS-4

Solute	PEGA		PPMS-4	
	ΔS_i°	δS_i°	ΔS_i°	δS_i°
Toluene	-0.84	0.04	-	-
<i>o</i> -Xylene	-2.00	0.01	-	-
<i>m</i> -Xylene	-1.97	-0.14	-	-
<i>p</i> -Xylene	-1.76	-0.07	-	-
1,2,3-Trimethylbenzene	-2.89	-0.02	-	-
1,2,4-Trimethylbenzene	-2.86	-0.22	-	-
1,3,5-Trimethylbenzene	-3.06	-0.47	-	-
1,2,4,5-Tetramethylbenzene	-3.79	-0.30	-	-
1,2,3,5-Tetramethylbenzene	-3.67	-0.16	-	-
Chlorobenzene	-0.76	0.87	-1.63	0.17
<i>p</i> -Dichlorobenzene	-2.31	0.59	-2.87	0.26
<i>m</i> -Dichlorobenzene	-2.18	0.78	-2.90	0.34
<i>o</i> -Dichlorobenzene	-2.45	0.81	-2.86	0.48
1,3,5-Trichlorobenzene	-3.41	0.60	-3.97	0.43
1,2,4-Trichlorobenzene	-4.18	0.49	-4.57	0.09
1,2,3-Trichlorobenzene	-3.94	0.69	-4.49	0.38
1,2,3,5-Tetrachlorobenzene	-5.30	0.14	-5.88	0.03
1,2,4,5-Tetrachlorobenzene	-5.28	0.20	-5.93	-0.02
1,2,3,4-Tetrachlorobenzene	-5.56	0.18	-6.11	0.12
<i>o</i> -Chlorotoluene	-1.92	0.53	-2.32	0.32
<i>m</i> -Chlorotoluene	-2.33	0.28	-2.45	0.24
<i>p</i> -Chlorotoluene	-2.32	0.15	-2.43	0.17
2,6-Dichlorotoluene	-3.57	0.27	-3.94	0.21
2,5-Dichlorotoluene	-3.72	0.21	-3.98	0.17
2,4-Dichlorotoluene	-3.62	0.22	-3.82	0.23
2,4,6-Trichlorotoluene	-4.51	0.17	-5.07	0.16
2,4,5-Trichlorotoluene	-4.79	0.29	-5.65	0.06
2,3,5-Trichlorotoluene	-4.80	0.31	-5.54	0.03
2,3,6-Trichlorotoluene	-4.77	0.34	-5.47	0.10
2,3,4-Trichlorotoluene	-5.20	0.26	-5.42	0.29
2,3,5,6-Tetrachlorotoluene	-5.54	0.59	-6.97	-0.10
2,3,4,5-Tetrachlorotoluene	-6.00	0.64	-7.27	-0.05
Pentachlorotoluene	-7.06	0.25	-8.45	-0.09
<i>o</i> -Chloro- <i>p</i> -xylene	-2.98	0.25	-3.86	-0.16
2,3-Dichloro- <i>p</i> -xylene	-3.83	0.69	-5.45	0.31
2,5-Dichloro- <i>p</i> -xylene	-4.42	0.23	-5.30	0.04
2,3,5-Trichloro- <i>p</i> -xylene	-5.30	0.39	-6.70	-0.13

ary phase^{7,8} for calculating relative molar enthalpies and entropies of solution in non-polar stationary phases.

Relative molar heats of solution in non-polar stationary phases, the difference between relative molar heats of solution in polar and non-polar stationary phases and relative molar entropies of solution in non-polar stationary phases are parameters for the identification of the substances under study by GLC. The relative molar heat of solution in Apiezon L is the most informative parameter for evaluating the number of substituents in the benzene ring, using eqns. 3-6. By comparing the δH_s° values (eqn. 8), it is possible to estimate the nature of the substituents, their homogeneity and the shielding of methyl groups. The relative molar entropy of solution in Apiezon L is the most informative parameter regarding the positions of substituents in the benzene ring; this parameter also gives information about the number of substituents in the molecule. It should be noted that the more reliable parameter for identification is relative molar heat of solution, which does not depend on the variation of some of the experimental conditions. Relative retentions for aromatic solutes are given in Table VII.

RELATIVE MOLAR ENTROPIES AND ENTHALPIES OF SOLUTION FOR OLEFINS

The experimental results are presented in Table VIII. Each relative value characterizes a change in the thermodynamic function of an olefin compared with a homomorphous alkane, *i.e.*, it indicates the influence of a double bond on the formation of the corresponding thermodynamic property. This pair of substances have similar configurations, which makes it possible to postulate a similar energy of hole formation during solution of these solutes. Hence, the relative molar heat of solution expresses only a variation in the energy of intermolecular forces.

We can assume that one of the major factors governing the relative molar heats of solution of isoolefins in pentadecane is an increase in the energy of the dispersion interaction when the methyl group is located in the α -position to the double bond. It is similar to the case of "hyperconjugation" for methylbenzenes. Let us denote the number of methyl groups in the α -position to the double bond by N and plot this value *versus* the relative molar heats of solution for isoolefins in pentadecane (Fig. 4). This relationship is linear and can be approximated by the equation (in kcal/mole)

$$\Delta H_s^\circ = 0.2 - 0.27N \quad (23)$$

Using these regularities, one can explain, for example, an increase in the relative molar heat of solution of 2-olefins compared with 1-olefins ($N = 0$ for 1-olefins and $N = 1$ for 2-olefins).

On dissolving olefins in a polar stationary phase, the orientation forces appear in the solution and therefore for these systems one should take into account an increase in the dispersion and orientation energies for each methyl group in the α -position to the double bond. Every double bond forms a dipole with the α -carbon atom, but only the α -methyl group is not a shielded part of the dipole. For dinitriloadipate, the experimentally found relative molar heats of solution are represented by the following equation (Fig. 5):

$$\Delta H_s^\circ = -0.25 - 0.38N \quad (24)$$

TABLE VII

RELATIVE RETENTIONS OF THE SOLUTES

The standard temperature for alkylbenzenes is 100° and for chloro derivatives 150°.

<i>Solute</i>	<i>Apiezon L</i>	<i>PPMS-4</i>
Toluene	2.12	—
<i>o</i> -Xylene	5.60	—
<i>m</i> -Xylene	4.71	—
<i>p</i> -Xylene	4.68	—
1,2,3-Trimethylbenzene	14.0	—
1,2,4-Trimethylbenzene	11.71	—
1,3,5-Trimethylbenzene	10.30	—
1,2,4,5-Tetramethylbenzene	29.3	—
1,2,3,5-Tetramethylbenzene	30.8	—
Pentamethylbenzene	94.8	—
Hexamethylbenzene	314	—
Chlorobenzene	2.85	2.97
<i>o</i> -Dichlorobenzene	9.17	8.27
<i>m</i> -Dichlorobenzene	7.70	7.22
<i>p</i> -Dichlorobenzene	7.70	7.32
1,3,5-Trichlorobenzene	15.3	15.35
1,2,4-Trichlorobenzene	19.2	16.5
1,2,3-Trichlorobenzene	24.5	21.8
1,2,3,5-Tetrachlorobenzene	42.2	34.9
1,2,4,5-Tetrachlorobenzene	45.0	33.9
1,2,3,4-Tetrachlorobenzene	57.9	47.0
Pentachlorobenzene	113.5	88.2
Hexachlorobenzene	437	221
<i>o</i> -Chlorotoluene	5.32	5.06
<i>m</i> -Chlorotoluene	5.34	4.78
<i>p</i> -Chlorotoluene	5.36	4.79
2,6-Dichlorotoluene	13.3	12.4
2,5-Dichlorotoluene	13.35	12.15
2,4-Dichlorotoluene	13.35	11.8
2,4,6-Trichlorotoluene	32.5	22.8
2,4,5-Trichlorotoluene	35.7	28.9
2,3,5-Trichlorotoluene	35.0	29.0
2,3,6-Trichlorotoluene	36.7	29.9
2,3,4-Trichlorotoluene	43.7	36.7
2,3,5,6-Tetrachlorotoluene	89.2	65.2
2,3,4,5-Tetrachlorotoluene	107	86.1
Pentachlorotoluene	229	186
<i>o</i> -Chloro- <i>p</i> -xylene	9.30	8.13
2,3-Dichloro- <i>p</i> -xylene	26.2	25.4
2,5-Dichloro- <i>p</i> -xylene	22.4	20.4
2,3,5-Trichloro- <i>p</i> -xylene	64.1	54.3

The first term on the right hand side of eqn. 24 expresses the additional energy of the electrostatic interaction for the shielded dipole formed by the double bond and a methylene group in the α -position. The numerical factor 0.38 represents the additional energy of the orientation forces. The mean standard deviation in the calculations of the relative molar heats of solutions using eqns. 23 and 24 is 0.1 kcal/mole.

Let us discuss the entropic selectivity for olefins (F values). The F values for isoolefins in pentadecane are described by the following linear relationship with the

TABLE VIII

RELATIVE MOLAR ENTHALPIES (kcal/mole) AND ENTROPIES OF SOLUTION (e.u.) FOR OLEFINS USING HOMOMORPHOUS ALKANE AS STANDARD

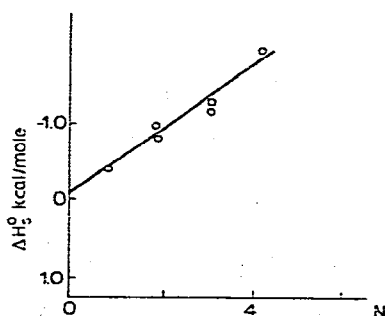
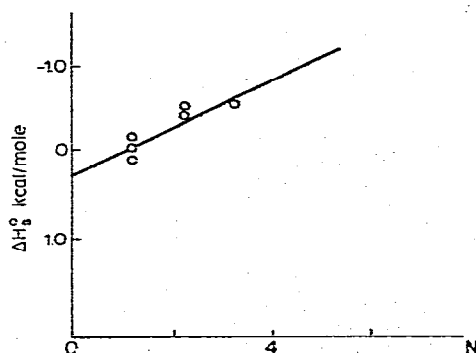
Olefin	<i>n</i> -Pentadecane			Dinitriloadipate		
	ΔH_s°	ΔS_s°	<i>F</i>	ΔH_s°	ΔS_s°	<i>F</i>
Propene	—	0.74	0.30	—	-0.11	0.51
Butene-1	—	0.66	0.22	—	—	—
Pentene-1	—	0.55	0.14	—	-0.25	0.34
Hexene-1	—	0.41	0.04	—	-0.31	0.28
<i>trans</i> -Pentene-2	—	-0.19	-0.09	—	-0.90	0.13
<i>cis</i> -Pentene-2	—	-0.39	-0.17	—	-1.14	0.11
<i>trans</i> -Hexene-2	—	-0.05	-0.05	—	-0.67	0.14
<i>cis</i> -Hexene-2	—	-0.14	-0.07	—	-0.98	0.17
<i>trans</i> -Hexene-3	—	0.06	0.01	—	-0.67	0.14
<i>cis</i> -Hexene-3	—	0.01	-0.06	—	-1.01	0.11
3-Methylbutene-1	0.17	0.03	-0.22	—	—	—
2-Methylbutene-2	-0.53	-0.85	-0.07	-1.21	-1.57	0.21
3-Methylpentene-1	0.07	-0.17	-0.07	—	-0.83	-0.07
4-Methylpentane-1	0.23	+0.12	-0.22	-0.20	—	—
<i>trans</i> -4-Methylpentene-2	-0.10	-0.36	-0.21	-0.55	-0.84	-0.03
<i>cis</i> -4-Methylpentene-2	0.03	-0.18	-0.22	-0.52	-0.72	0.04
2-Methylpentane-1	-0.15	-0.24	-0.02	-0.90	-1.25	0.07
<i>trans</i> -3-Methylpentene-2	-0.40	-0.70	-0.11	—	—	—
3,3-Dimethylbutene-1	0.30	-0.05	-0.45	-0.25	-0.22	0.16
2,3-Dimethylbutene-1	0.04	0.03	-0.03	-0.60	-0.77	0.11
2,3-Dimethylbutene-2	-0.88	-1.57	-0.28	—	—	—

number of carbon atoms in the molecule (*C*):

$$F = 0.55 - 0.08C \quad (25)$$

The limit of the *F* value is zero (Fig. 6).For the systems under study, $\ln M^\circ$ is about zero, and therefore we can write

$$F = c'R \ln J^\circ/\sigma^\circ \quad (26)$$

Fig. 4. Relationship between the relative molar heats of solution for olefins in pentadecane and their *N* values.Fig. 5. Relationship between the relative molar heats of solution for olefins in dinitriloadipate and their *N* values.

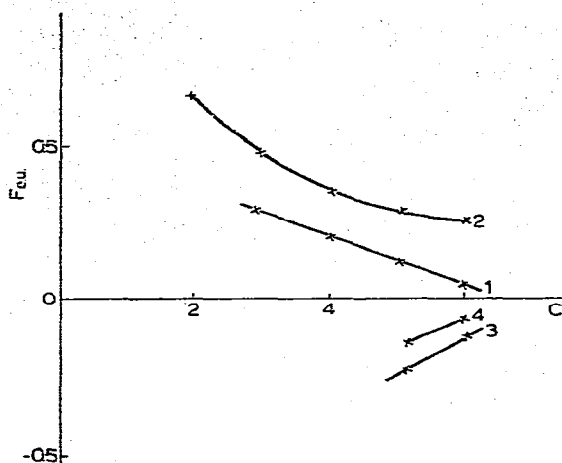


Fig. 6. Relationships between F values and number of carbon atoms in n -olefin molecules. 1, 1-Olefins in pentadecane; 2, 1-olefins-1 in dinitriloadipate; 3, *cis*-olefins in pentadecane; 4, *trans*-olefins in pentadecane.

The effective diameter of the hole in the n -alkane stationary phase is about 3.7 Å (ref. 14), and therefore rotation of propane and propene molecules along the A-A' axis (Fig. 7) in this hole is not hindered, but rotation along the two remaining axes is partially hindered. For the given pair of molecules, the $R\ln J^\circ$ value along the last two axes is 0.45 e.u. and $R\ln\sigma^\circ$ is -2.75 e.u. Then, from eqn. 26, $c' = 0.094$. This value is higher than that for aromatic solutes in Apiezon L because of the difference in the temperatures of the experiments (25° and 100°).

Thus, the calculation on the basis of geometric parameters permits correct conclusions about the relative molar entropies of olefins to be drawn. The possibility of making similar calculations for high-molecular-weight olefins is slight as it is impossible to change the proper configuration of a molecule in the gas phase. Energetic considerations suggest that a spherical conformation is favourable. In such spherical molecules, the differences between saturated and unsaturated hydrocarbons disappear, and therefore the F values tend to zero (Fig. 6).

The molecules of *trans*-olefins (normal) have the same isotactic configuration as the homomorphous alkanes, and therefore their F values are close to zero. The structure of *cis*-olefins (normal) is non-isotactic and therefore their F values are negative (Fig. 6).

When dissolving a substance in a polar stationary phase one should take into consideration not only its solubility but also a marked contribution to the retention volume of adsorption on the interphase boundaries.

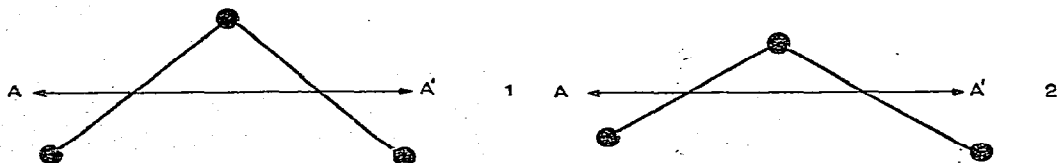


Fig. 7. Models of propane (1) and propene (2) molecules.

When a polar stationary phase is used, not only the entropy of the external rotation is decreased but also the internal rotation is decreased. In olefin molecules, the internal rotation around the double bond is fully hindered, and hence the variation of the internal entropy during solution is lower for olefins than that for homomorphous alkanes. The limit of this difference is about 0.2 e.u. (Fig. 6).

Our results show that it is possible to calculate the relative molar heats of solutions for olefins in non-polar and polar stationary phases, and these calculated values can be useful for identification purposes in GLC.

CONCLUSIONS

It has been shown that the proposed semi-empirical theory of selectivity of the stationary phase permits one to calculate the enthalpic selectivity for chloro- and methyl-substituted benzenes and C₅-C₆ olefins with a mean standard deviation of about 0.1 kcal/mole and the entropic selectivity for these aromatic solutes with a mean standard deviation of 0.2 e.u. using a non-polar stationary phase. It is possible to identify the number of substituents and their homogeneity using the relative molar heats of solution in the non-polar stationary phase and the difference between molar heats of solution in polar and non-polar stationary phases. The relative molar entropy of the aromatic solutes is a useful value for estimating the positions of substituents in the benzene ring.

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