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SELECTIVITY OF STATIONARY PHASES FOR SOME POLAR BENZENE DERIVATIVES

A. N. KOROL

Institute of Physical Chemistry, pr. Nauki 31, Kiev, 252028 (U.S.S.R.)

and

N. V. NOVORUSSKAYA

Institute of Monomers, ul. Lenina 106, Tula (U.S.S.R.)

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SUMMARY

Relative retentions and molar heats of solution of some oxygen and chloro benzene derivatives were determined. Influences of column length and life, and amount of the stationary phase on the retention data are established. The molar heats of solution are discussed taking into account mesomeric and inductive effects of the substituents in the benzene ring.

INTRODUCTION

The selectivity of some stationary phases for simple benzene derivatives was discussed previously¹. It is of interest to extend that study to more complex derivatives, which exhibit new combinations of mesomeric and inductive effects. These properties complicate the calculations of the stationary phase selectivity^{2,3}. Although these substances are of industrial importance, few studies^{4,5} of them have been concerned with selectivity, most reports⁶⁻¹⁰ being restricted to analytical problems.

The aim of the present study was the determination of retention data for complex benzene derivatives, in order to find some trends which could be employed in the calculation of the stationary phase selectivities; the interphase adsorption^{11,12} has been taken into account.

EXPERIMENTAL

The retention data were determined on a Fractovap Model 2200 chromatograph equipped with a flame ionization detector. Glass columns (0.7-1.1 m long) were packed with Chromaton N AW HMDS (Lachema, Brno, Czechoslovakia) as the support and 10% of the stationary phase. All the packings were conditioned at 190° for 25-30 h.

TABLE I

DEPENDENCE OF RETENTION DATA ON COLUMN LENGTH

Stationary phase, PEGA; relative retention at 170°; Δ = the difference between the values on the two columns.

Solute	$\log r$			ΔH_s^0 (kcal/mole)		
	0.7 m	1.05 m	Δ	0.7 m	1.05 m	Δ
Methyl benzoate	-0.195	-0.197	0.002	0.08	0.10	0.02
Methyl <i>o</i> -toluate	-0.069	-0.077	-0.008	-0.54	-0.69	-0.15
Methyl <i>m</i> -toluate	0.014	0.010	-0.004	-0.92	-0.80	0.12
Methyl <i>p</i> -toluate	0.027	0.027	0	-0.69	-0.79	-0.10
Methyl 2,5-dimethylbenzoate	0.121	0.120	-0.001	-1.30	-1.30	0
Methyl 2,4-dimethylbenzoate	0.145	0.145	0	-1.30	-1.30	0
Methyl 3,4-dimethylbenzoate	0.329	0.333	0.004	-1.97	-1.58	0.39
Dimethyl terephthalate	0.878	0.890	0.012	-3.54	-3.36	0.18
<i>o</i> -Methylbenzaldehyde	-0.168	-0.174	-0.006	0.17	0.17	0
<i>p</i> -Methylbenzaldehyde	-0.118	-0.121	-0.003	0.10	0.21	0.11
<i>p</i> -Isopropylbenzaldehyde	0.112	0.109	-0.003	-1.08	-0.94	0.14
2- <i>p</i> -Tolyl-2-propanol	0.146	0.158	0.012	-1.64	-1.65	-0.01
Benzyl alcohol	0.137	0.138	0.001	-1.29	-1.36	-0.07
<i>p</i> -Toluic alcohol	0.300	0.305	0.005	-2.24	-1.96	0.28
<i>o</i> -Toluic alcohol	0.344	0.356	0.012	-2.18	-2.09	0.09
Cuminol	0.528	0.534	0.006	-2.86	-2.79	0.07
Phthalaldehyde	0.658	0.648	-0.010	-2.56	-1.82	0.74
Terephthalaldehyde	0.643	0.639	-0.004	-2.42	-1.85	0.67

The relative standard deviations of the relative retention r were 0.25, 0.5 and 0.8% for chlorinated benzene derivatives, alkylbenzenes and complex benzene derivatives, respectively. Molar heats of solution, ΔH_s , and relative molar heats of solution, ΔH_s^0 , were calculated as in ref. 13. The relative retentions at standard temperatures (100° C for alkylbenzenes and 150° C for other solutes) were calculated from the relationships between $\log r$ and $1/T$. The mean standard deviation of the molar heat of solution was 0.07 kcal/mole.

The specific retention volumes, V_g , were calculated as described elsewhere¹⁴. The amount of stationary phase in the column, w_L , was determined by weighing the packing in the column; this value was then corrected for losses of the stationary phase on conditioning. The relative mean standard deviation of V_g was *ca.* 3%.

Five liquids were selected as the stationary phases: Apiezon L (non-polar), polyethylene glycol sebacate (PEGS), polyethylene glycol adipate (PEGA, polar), 5-ring poly(phenyl ether) (PPE) and silicone OV-17 (structure-selective).

RETENTION DATA AND LIFETIME AND LENGTH OF THE COLUMNS

The dependence of retention data on column length¹⁵ is shown in Table I.

Some deviations of retention indices on column ageing have been reported^{16,17}. The present experiments were carried out using the PEGS column; retention data were determined for three years whilst the column was used for the separation of different polar benzene derivatives. The results show that the deviations in $\log r$ do

not exceed 0.01, this value being close to the experimental error. The mean standard deviation of the ΔH_S^0 value for the same period is 0.16 kcal/mole, which is twice the experimental error. The maximum deviations of ΔH_S^0 were observed during the second year of column use. These data show that columns older than one year should not be used for determining the ΔH_S^0 data.

DEPENDENCE OF RETENTION DATA ON THE AMOUNT OF STATIONARY PHASE

The stationary phase exists on the support in two different states: as the bulk (capillary) liquid and as the adsorption layer¹⁸; the liquid in these two states has different distribution coefficients $K_L^c < K_L^a$ (ref. 19), whereas the superscripts *c* and *a* denote the capillary and adsorbed liquids, respectively. If V_N is the net retention volume related to the solubility and V_L is the volume of the stationary phase, we can write:

$$V_N^s = K_L^c V_L^c + K_L^a V_L^a \quad (1)$$

Substituting K_L by V_g , we obtain

$$273.2 \cdot V_N^s / T = V_g^c w_L^c + V_g^a w_L^a \quad (2)$$

and hence

$$\frac{273.2 \cdot V_N^s}{T \cdot w_L} = V_g = \frac{V_g^c w_L^c}{w_L} + \frac{V_g^a w_L^a}{w_L} \quad (3)$$

and

$$V_g^* = \frac{V_g^c w_L^c}{w_L} + \frac{V_g^a w_L^a}{w_L} + \frac{K_a^{sL} S^{sL} \cdot 273.2}{w_L T} + \frac{K_a^{gL} S^{gL} \cdot 273.2}{w_L T} \quad (4)$$

where V_g^* is the effective retention volume, measured under gas-liquid chromatographic (GLC) conditions, the superscripts *sL* and *gL* relate to the solid-liquid and gas-liquid interphases, respectively, *S* is the interphase surface area and K_a is the adsorption distribution coefficient.

When w_L is increased, w_L^a raises to a constant value since the influence of the support is limited by distance; usually, w_L^a becomes constant at $w_L \geq 10\%$. After wetting the whole support area ($w_L \geq 1-3\%$), the solid-liquid interphase area is constant and the gas-liquid interphase area decreases with increasing w_L (refs. 11, 12). Since the adsorption terms in eqn. 4 decrease with increasing w_L , the value of V_g^* also decreases (Figs. 1-4). At a certain value of w_L , the numerators of the last three terms in the right-hand side of eqn. 4 become approximately constant while w_L^c increases rapidly; moreover, since $K_L^c < K_L^a$, the value of V_g^* increases with w_L . A combination of these processes results in the appearance of a minimum in the relationship between V_g^* and w_L (see Figs. 1-4).

When Apiezon L is used as the stationary phase the minimum appears at $w_L = 25\%$; the difference in the values of V_g^* for packings containing 40 and 25% stationary phase is ca. 5-8%, in accordance with literature data^{15,19}. The left-hand side of the graphs in Figs. 1-4 yields the interphase adsorption^{11,12}. The right-hand

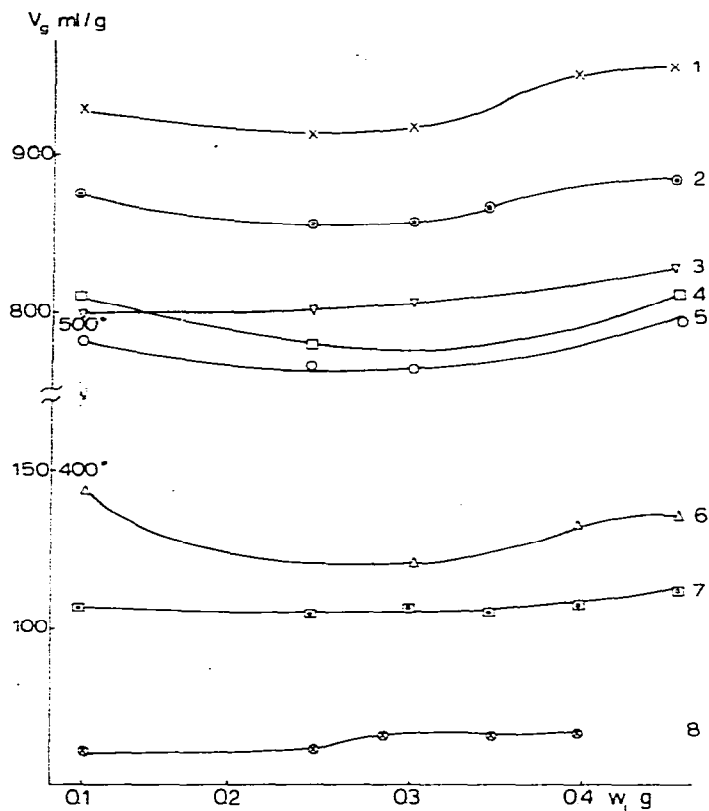


Fig. 1. Dependence of V_g on the amount of Apiezon L in the column. 1 = Naphthalene; 2 = phthalaldehyde; 3 = methyl *p*-toluate; 4 = dimethyl isophthalate; 5 = dimethyl phthalate; 6 = benzoic acid; 7 = *p*-methylbenzaldehyde; 8 = benzyl alcohol. V_g values for curve 4 are those to the right of the vertical axis.

side of the graphs yields the apparently negative adsorption values for high loadings when the calculations are made using the relationships between V_g^* and $1/w_L$ (Table II). These values have no physical meaning. The only useful information is obtained by extrapolating the relationships to $1/w_L = 0$ which yields the real V_g values. Unfortunately, the extrapolated data have a relatively large error (*s ca.* 7%).

When using the polar stationary phases the adsorption at gas-liquid interphase is of great importance, and the decrease of S^{gl} with increasing w_L has a greater influence on V_g^* than for non-polar packings. Therefore, the slope of the adsorption curve is greater for polar than for non-polar packings, and the minimum in the curves is shifted to lower w_L values. The minimum for the poly(phenyl ether) packing is shifted to a high w_L value (35–38%), enabling the adsorption to be calculated more precisely.

The minimum in the relationship between V_g^* and w_L allows one to recommend the w_L value which corresponds to the minimum as a standard amount of the stationary phase and thus obtain better interlaboratory reproducibility of the retention data. Indeed, some deviations of w_L cannot influence the retention data at the recommended conditions.

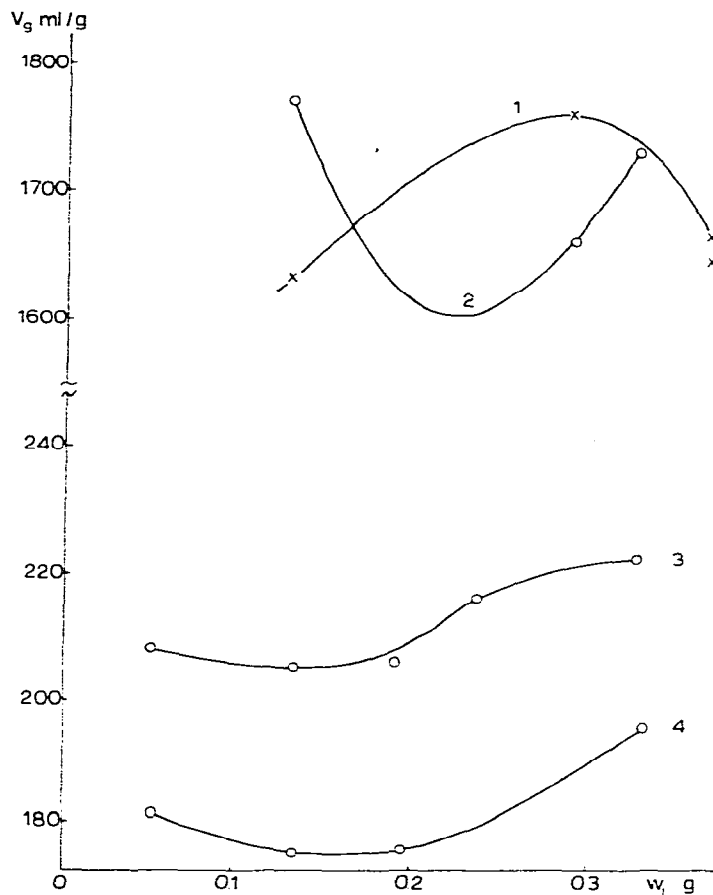


Fig. 2. Dependence of V_g on the amount of PEGA in the column. 1 = Dimethyl phthalate; 2 = dimethyl isophthalate; 3 = benzoic acid; 4 = *p*-methylbenzaldehyde.

MOLAR HEATS OF SOLUTION

The first difficulty in a discussion of the experimental molar heats of solution ΔH_{se} is the necessity of taking into account the interphase adsorption²⁰. When using the packings with $w_L \geq 10\%$, the interphase adsorption changes the value of the molar heat of solution by $\geq 5\%$ on this value being close to the experimental error.

The experimental molar heat of solution may be expressed² as

$$\Delta H_{se} = \Delta H_{sc} + \Delta H_h + E_c + RT \quad (5)$$

where ΔH_{sc} is the molar heat of solution related to the dispersion interaction energy, and is calculated from the dispersion index D_n and shielding coefficient K_n for each atomic group in the solute molecule using the additivity principle

$$\Delta H_{sc} = i \sum_n K_n D_n,$$

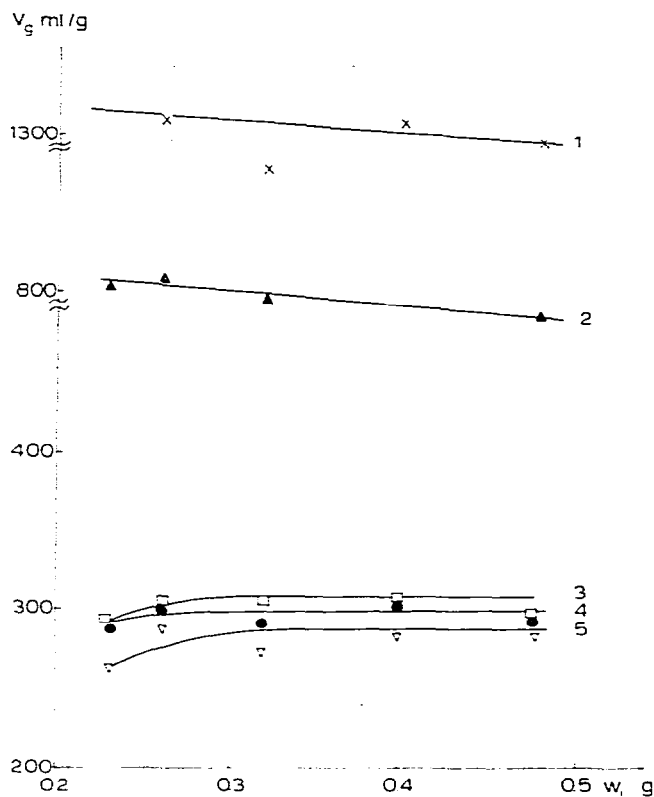


Fig. 3. Dependence of V_g on the amount of PEGS in the column. 1 = Benzoic acid; 2 = cuminol; 3 = naphthalene; 4 = benzyl alcohol; 5 = methyl *p*-toluate.

where i is a normalization factor. ΔH_h is the molar heat of hole formation, E_c is the concentration effect for polar solutes²¹, R is the gas constant and T is the column temperature in $^{\circ}\text{K}$.

It has been shown¹ that for aromatic hydrocarbons two additional terms are required in eqn. 5, *i.e.*, 0.7 kcal/mole, related to the interaction with the benzene ring, and $-0.6 n_{\text{CH}_3}$ (n_{CH_3} is the methyl group number in the molecule). Taking into account the fact that E_c for aromatic hydrocarbons is approximately zero, the ΔH_h values for these solutes were calculated by using ΔH_{se} (Table III). The aromatic hydrocarbons are used as the homomorphous substances for the polar solutes: for example, *n*-propylbenzene is the homomorph for methyl benzoate, and toluene is the homomorph for chlorobenzene. It is assumed that homomorphous substances have the same ΔH_h value.

The E_c term was calculated for the polar solutes using eqn. 5 and these values have a strict physical meaning²². The data in Table III show that the average values of E_c are -0.25 , -1.5 and -2.8 kcal/mole for chlorobenzenes, aldehydes and methyl esters, and alcohols, respectively. For the corresponding derivatives of aliphatic hydrocarbons, the values are -1.1 , -0.7 and -3.0 kcal/mole (ref. 21). The differences in these values may be explained in terms of the different electron cloud distributions in these solute molecules.

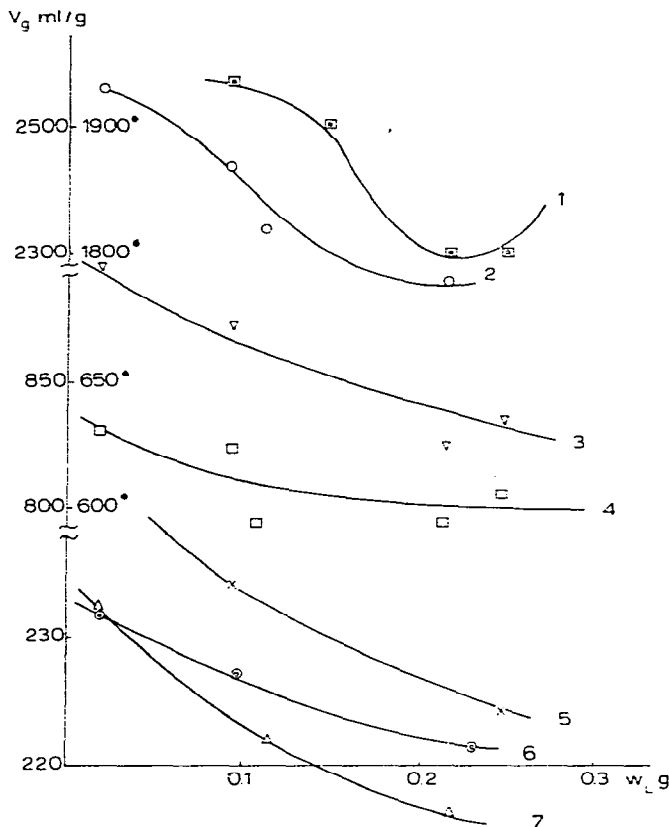


Fig. 4. Dependence of V_g on the amount of PPE in the column. 1 = Dimethyl phthalate; 2 = dimethyl isophthalate; 3 = phthalaldehyde; 4 = cuminol; 5 = naphthalene; 6 = benzoic acid; 7 = benzyl alcohol. V_g values for curves 1 and 4 are those to the right of the vertical axis.

The concentration effect E_c is dependent on the associative ability of the solute molecules. Except for hydrogen bonds, this effect is proportional to the dipole moment of the molecule. When a given substituent is bound to an aliphatic chain only an induction effect is observed, while a mesomeric effect occurs for aromatic radicals. Methyl, methoxy, chloro and hydroxyl groups have positive mesomeric effects, *i.e.*, they increase the π -electron density in the benzene ring. Esters and carbonyl groups have negative mesomeric effects. By comparing the dipole moments for the same polar groups in different radicals (Table IV) one can see the influence of the mesomeric effect on the dipole moment of the solute molecule: polar groups with positive mesomeric effects decrease the dipole moment. The influence of the nature and number of the substituents on the E_c values will now be discussed.

Monosubstituted derivatives

Let us suppose that the orientation forces in GLC solutes occur only between microdipoles of small atomic groups²³. For aromatic solutes one can consider the positive pole of the dipole to be delocalized along the benzene ring while the negative

TABLE II

EFFECT OF THE AMOUNT OF STATIONARY PHASE ON THE COLUMN RETENTION DATA

V_g^x is the value of V_g extrapolated to a column containing an infinite amount of the stationary phase; δ is the ratio $(V_g^m - V_g^x)/V_g^x$, where V_g^m is the minimum value of the specific retention volume.

Solute	V_g (ml/g)							V_g^x	δ
	Amount of Apiezon L in column (g)								
	0.436	0.378	0.331	0.286	0.232	0.103			
Naphthalene	276	274	—	258	255	263	298	-17	
<i>p</i> -Methylbenzaldehyde	112	108	105	107	104	106	116	-12	
Benzyl alcohol	—	66.8	66.5	—	62.3	—	68	-10	
Methyl <i>p</i> -toluate	214	—	—	203	201	198	207	-3	
Phthalaldehyde	240	—	232	228	226	237	251	-11	
Benzoic acid	136	133	—	120	—	143	163	-10	
Dimethyl isophthalate	810	—	—	759	779	808	790	-2	
Dimethyl phthalate	491	—	—	463	462	480	490	-6	
	Amount of poly(phenyl ether) in column (g)								
	0.453	0.448	0.418	0.314	0.297	0.223			
Naphthalene	365	—	—	—	374	385	345	10	
<i>p</i> -Methylbenzaldehyde	221	—	215	—	227	232	211	10	
Benzyl alcohol	171	171	167	172	181	182	156	14	
Phthalaldehyde	837	—	825	—	873	890	785	11	
Cuminol	—	615	587	588	624	632	595	5	
Dimethyl phthalate	—	1800	1800	—	1930	1945	1845	5	
Dimethyl isophthalate	—	2345	2260	2340	2470	2555	2140	16	
	Amount of PEGS in column (g)								
	0.471	0.398	0.319	0.262	0.234	V_g^x	δ		
Naphthalene	301	310	308	305	292	316	-8		
<i>p</i> -Methylbenzaldehyde	198	198	191	187	201	210	-12		
Benzyl alcohol	287	287	273	289	267	297	-11		
Methyl <i>p</i> -toluate	297	305	291	303	294	312	-8		
Cuminol	788	—	800	811	809	760	11		
Benzoic acid	1300	1312	1282	1314	1366	1280	6		
Dimethyl isophthalate	1900	1905	1825	1954	1898	1900	0		
Dimethyl phthalate	1580	1590	1580	1575	—	1590	-1		
	Amount of PEGA in column (g)								
	0.372	0.280	0.233	0.192	0.127	0.070	V_g^x	δ	
Naphthalene	—	—	217	206	204	208	240	-17	
<i>p</i> -Methylbenzaldehyde	—	—	170	158	156	166	186	-19	
Benzyl alcohol	294	296	299	297	—	300	302	-2	
Methyl <i>p</i> -toluate	228	—	—	217	217	224	243	-12	
Phthalaldehyde	914	928	923	886	873	975	950	-9	
Dimethyl isophthalate	1667	1657	—	—	1636	1741	1695	-4	

pole is located on some heteroatom (for example, chlorine, oxygen, etc.). Because the orientation forces are proportional to the square of dipole moment is a relationship between E_c and μ^2 is observed for monosubstituted polar benzene derivatives (Fig. 5). The points for anisole, chlorobenzene and benzaldehyde lie on a straight

TABLE III
MOLAR HEATS OF SOLUTION OF THE SOLUTES ON APIEZON L (KCAL/MOLE)
 $K_n D_n$ data are listed in relative units, i data in kcal/mole.

<i>Solute</i>	$\Sigma K_n D_n$	$-i$	$-\Delta H_{sc}$	$-\Delta H_{sc}$	ΔH_h	E_c
Benzene	15.5	0.454	7.04	6.34	0	—
Toluene	18.45	0.448	8.28	7.34	0.84	—
Ethylbenzene	21.0	0.444	9.35	9.13	0.51	—
<i>n</i> -Propylbenzene	23.25	0.444	10.32	9.04	0.58	—
<i>n</i> -Butylbenzene	25.5	0.443	11.24	10.12	0.48	—
<i>o</i> -Xylene	21.3	0.447	9.52	8.65	1.37	—
<i>m</i> -Xylene	21.3	0.447	9.52	8.51	1.51	—
<i>p</i> -Xylene	21.3	0.447	9.52	8.51	1.51	—
<i>o</i> -Ethyltoluene	23.95	0.443	10.61	9.41	1.10	—
<i>m</i> -Ethyltoluene	23.95	0.443	10.61	9.33	1.18	—
<i>p</i> -Ethyltoluene	23.95	0.443	10.61	9.28	1.23	—
1,2,3-Trimethylbenzene	24.2	0.442	10.85	9.90	0.95	—
1,2,4-Trimethylbenzene	24.2	0.442	10.85	9.63	2.32	—
1,3,5-Trimethylbenzene	24.2	0.442	10.85	9.66	2.29	—
1,2-Diethylbenzene	26.5	0.442	11.71	10.35	1.36	—
1,3-Diethylbenzene	26.5	0.442	11.71	10.15	0.86	—
1,4-Diethylbenzene	26.5	0.442	11.71	10.25	0.76	—
Isopropylbenzene	25.35	0.445	11.28	8.76	1.82	—
<i>p</i> -Isopropyltoluene	28.3	0.445	12.59	10.0	2.49	—
1,4-Diisopropylbenzene	35.2	0.445	15.66	11.0	3.96	—
1-Ethyl-4-isopropylbenzene	28.0	0.445	12.55	11.05	0.80	—
1,2,4,5-Tetramethylbenzene	27.1	0.447	12.15	10.88	2.97	—
Pentamethylbenzene	30.0	0.447	13.4	12.42	3.32	—
Hexamethylbenzene	32.9	0.447	14.75	13.95	3.70	—
Chlorobenzene	20.6	0.456	9.40	8.10		-0.25
1,2-Dichlorobenzene	24.8	0.462	11.6	9.35		0
1,3-Dichlorobenzene	24.8	0.462	11.6	9.30		0
1,4-Dichlorobenzene	24.8	0.462	11.60	9.30		0
<i>o</i> -Chlorotoluene	22.7	0.46	10.45	8.85		-0.14
<i>m</i> -Chlorotoluene	22.7	0.46	10.45	8.85		0
<i>p</i> -Chlorotoluene	22.7	0.46	10.45	8.85		0
Methyl benzoate	24.1	0.445	10.72	11.05		-1.60
Methyl <i>o</i> -toluate	27.05	0.445	12.04	11.85		-1.39
Methyl <i>m</i> -toluate	27.05	0.445	12.04	11.75		-1.57
Methyl <i>p</i> -toluate	27.05	0.445	12.04	11.75		-1.62
Methyl 2,5-dimethylbenzoate	30.0	0.445	13.35	12.45		-0.90
Methyl 2,4-dimethylbenzoate	30.0	0.445	13.35	12.50		-0.95
Methyl 3,4-dimethylbenzoate	30.0	0.445	13.35	13.05		-1.50
Methyl <i>p</i> -isopropylbenzoate	33.95	0.45	15.28	13.05		0.83
Dimethyl phthalate	32.7	0.45	14.72	13.30		0.07
Dimethyl isophthalate	32.7	0.45	14.72	14.05		-0.88
Dimethyl terephthalate	32.7	0.45	14.72	14.00		-0.72
Dimethyl methylterephthalate	35.65	0.45	16.04	14.85		-0.26
Dimethyl <i>o</i> -methylisophthalate	35.65	0.45	16.04	14.90		-0.31
Methyl <i>o</i> -chlorobenzoate	29.2	0.45	13.14	12.10		-0.66
Methyl 2,4-dichlorobenzoate	34.3	0.45	15.44	12.20		0.22
Methyl 2,5-dichlorobenzoate	34.3	0.45	15.44	12.30		0.12
Methyl 2,3,6-trichlorobenzoate	39.4	0.455	17.93	13.45		0.81
Methyl 3,6-dichloro-2-methoxybenzoate	40.1	0.455	18.24	12.30		2.27

(Continued on p. 82)

TABLE III (continued)

<i>Solute</i>	$\Sigma K_n D_n$	$-i$	$-\Delta H_{sc}$	ΔH_{sc}	E_c
Benzaldehyde	20.7	0.45	9.32	9.53	-1.51
Phthalaldehyde	25.9	0.45	11.65	11.70	-1.40
Isophthalaldehyde	25.9	0.45	11.65	11.80	-1.60
<i>o</i> -Methylbenzaldehyde	23.65	0.45	10.65	10.50	-2.52
<i>m</i> -Methylbenzaldehyde	23.65	0.45	10.65	10.55	-2.71
<i>p</i> -Methylbenzaldehyde	23.65	0.45	10.65	10.60	-2.76
2,5-Dimethylbenzaldehyde	26.60	0.45	11.97	11.35	-1.21
2,4-Dimethylbenzaldehyde	26.60	0.45	11.97	11.35	-1.21
3,4-Dimethylbenzaldehyde	26.60	0.45	11.97	11.80	-1.65
<i>p</i> -Cresyl acetate	29.50	0.45	13.27	11.15	0.19
Anisole	21.7	0.45	9.76	8.55	0
<i>o</i> -Chloroanisole	26.8	0.46	12.33	10.70	-0.17
<i>p</i> -Chloroanisole	26.8	0.46	12.33	10.45	-0.05
2,4-Dichloroanisole	31.9	0.46	14.67	12.80	-1.15
2,5-Dichloroanisole	31.9	0.46	14.67	12.45	-0.80
2,6-Dichloroanisole	31.9	0.46	14.67	11.00	0.92
2,4,5-Trichloroanisole	37.0	0.46	17.02	13.45	0.10
2,4,6-Trichloroanisole	37.0	0.46	17.02	12.15	1.30
2,3,5,6-Tetrachloroanisole	42.1	0.46	19.37	14.2	1.15
Pentachloroanisole	47.2	0.46	21.71	15.55	1.76
<i>o</i> -Tolyl acetate	32.15	0.45	14.47	12.15	1.12
<i>p</i> -Tolyl acetate	32.15	0.45	14.47	12.30	0.84
2,5-Dimethylbenzyl acetate	35.1	0.45	15.80	13.25	0.73
2,4-Dimethylbenzyl acetate	35.1	0.45	15.80	13.30	0.68
3,4-Dimethylbenzyl acetate	35.1	0.45	15.80	13.45	0.52
Benzyl alcohol	20.5	0.45	9.22	10.68	-2.76
<i>o</i> -Methylbenzyl alcohol	23.45	0.45	10.55	10.75	-2.87
<i>m</i> -Methylbenzyl alcohol	23.45	0.45	10.55	10.65	-2.90
<i>p</i> -Methylbenzyl alcohol	23.45	0.45	10.55	10.65	-2.90
3,4-Dimethylbenzyl alcohol	26.4	0.45	11.88	11.90	-1.74
2,4-Dimethylbenzyl alcohol	26.4	0.45	11.88	12.00	-1.94
2,5-Dimethylbenzyl alcohol	26.4	0.45	11.88	12.00	-1.94
<i>p</i> -Isopropylbenzaldehyde	30.55	0.45	13.75	11.85	0.40

TABLE IV

COMPARISON OF DIPOLE MOMENTS OF SOME ALIPHATIC AND AROMATIC COMPOUNDS

<i>Compound</i>	<i>Dipole moment (debyes)</i>	<i>Compound</i>	<i>Dipole moment (debyes)</i>
Chlorobenzene	1.6	<i>n</i> -Pentyl chloride	2.12
Benzaldehyde	2.95	<i>n</i> -Pentanal	2.57
Benzyl alcohol	1.67	<i>n</i> -Pentanol	1.55
Anisole	1.2	Methyl butyl ether	1.25
Methyl benzoate	1.9	Methyl propionate	1.7

line while the point for methyl benzoate deviates markedly from this line because the ester group has two microdipoles, one for the carbonyl oxygen and another for the ester oxygen. The presence of two microdipoles instead of one in a polar molecule markedly increases the orientation forces (in the case of an ester this increase is 1.1 kcal/mole). If the E_c value for an ether oxygen is 0 (this oxygen is strongly shielded

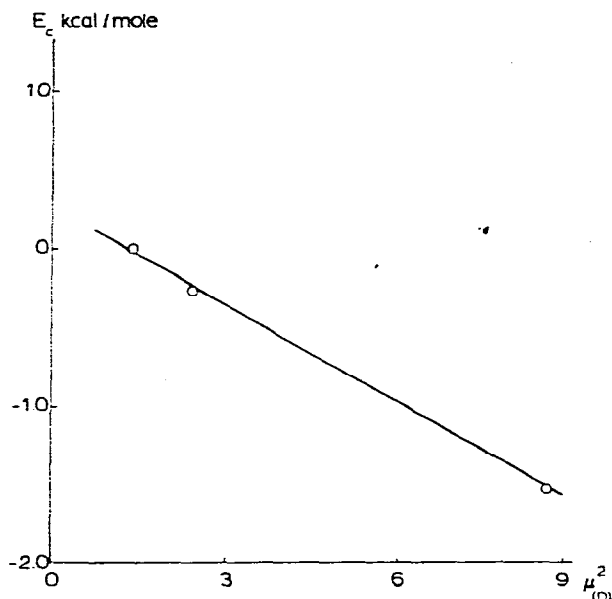


Fig. 5. Dependence of E_c on the square of the dipole moment of the solutes.

by the neighbouring atoms), the values for aldehydes and esters are nearly the same because only the carbonyl oxygen is accessible to orientation interaction.

The relationship illustrated in Fig. 5 verifies the assumptions made about the nature of the E_c concentration effect.

Disubstituted polar benzene derivatives

Table III shows that as the number of chlorine atoms in chlorobenzenes increases the E_c value decreases to 0. Despite the increasing C-Cl dipoles in the chlorobenzenes, the orientation forces become too small to produce any concentration effect; this fact may be related to the positive mesomeric effect of chlorine when the π -electron density in the benzene ring increases. The effect of a second substituent on E_c is dependent on the Van der Waals volume of this substituent. For example, no or little effect on E_c is observed for chlorotoluenes and chloroanisoles (Fig. 6).

Some decrease of E_c is seen when passing from mono- to disubstituted derivatives of methyl aldehydes and esters of methylbenzoic acid. Both the substituents, chloro and methyl group, have positive mesomeric effects, therefore, the difference between dichlorobenzenes, chlorotoluenes, chloroanisoles and methyl aldehydes, and methyl esters of methylbenzoic acid, is related to the sign of the mesomeric effect for the aldehyde and ester groups and the chloro and ether group. The aldehyde and ester groups "pump out" the π -electron cloud from the benzene ring, the additional π -electrons from the methyl group passing on to the substituent with a negative mesomeric effect; this process increases the molecular dipole and, therefore, the E_c value becomes more negative than that for monosubstituted benzene derivatives.

The final group of disubstituted benzene solutes are those in which both substituents exhibit negative mesomeric effects. These comprise the methyl esters of phthalic acids and dialdehydes. No significant effects are seen for series of aldehydes,

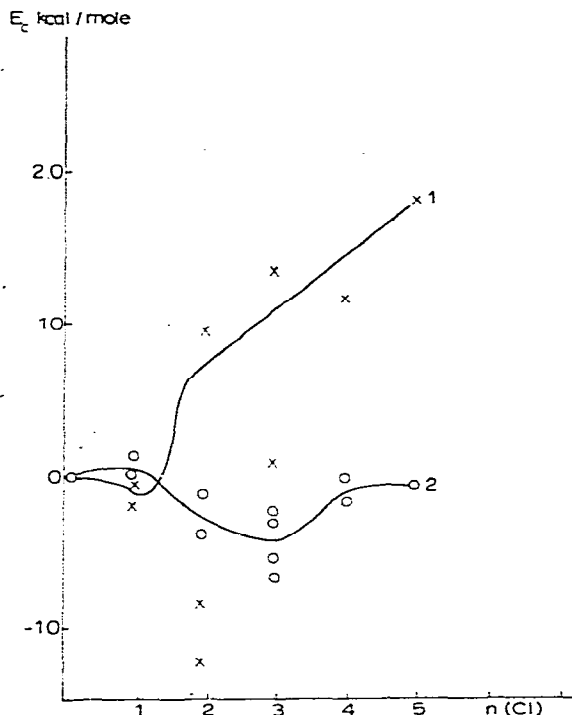


Fig. 6. Dependence of E_c on the number of chlorine atoms in the solute molecules. 1 = Chloroanisoles; 2 = chlorotoluenes.

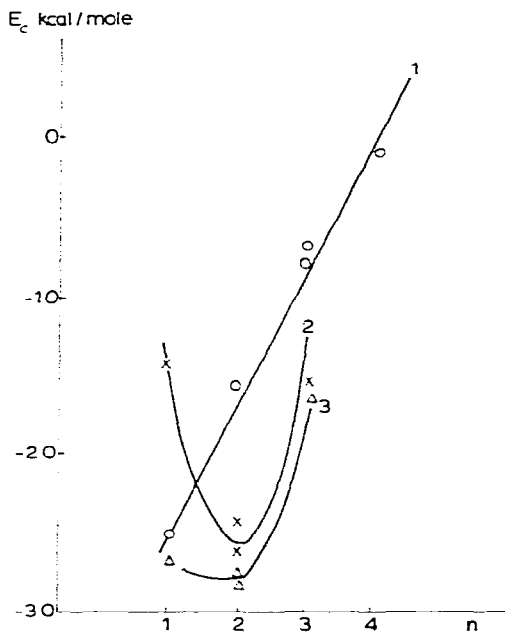


Fig. 7. Dependence of E_c on the number of substituents in the solute molecules. 1 = Methyl chlorobenzoates; 2 = methyl aldehydes; 3 = alcohols.

but for the methyl esters the E_c value increases markedly in passing from benzoic to phthalic acids. We conclude that when the mesomeric effect of the second substituent in a benzene ring exhibits the same sign as that of the first substituent, the E_c value changes little or increases.

Another factor which influences the E_c value is intramolecular shielding, which occurs when two substituents are placed *ortho* to each other. When the Van der Waals volumes of the two substituents are too large for them to be placed in *ortho* positions one of the substituents is no longer conjugated with the benzene ring (the benzene ring surface). This decreases the polarizability of the molecule and, hence, the intermolecular forces with the stationary phase. An example of this effect is found in the data for methyl ethers of phthalic acids substituted in the *o*-, *m*- and *p*-positions. The E_c values for the *o*-isomer are larger than these of the other two isomers by *ca.* 0.8 kcal/mole, owing to intramolecular shielding of two large substituents. The same effect may be seen on comparing the E_c values for isomeric dialdehydes, methyl derivatives of aldehydes, chlorotoluenes and chloroanisoles. The differences between the E_c values of the *o*-isomers and the other isomers depends on the Van der Waals radius of the substituent.

Polysubstituted polar benzene derivatives

The main influence on the E_c values of polysubstituted derivatives is the

intramolecular steric hindrance which occurs when substituents having large Van der Waals radii are no longer conjugated with the benzene ring. The best example of this is the methyl esters of chlorobenzoic acids (Fig. 7): here the dependence of E_c on the number of chlorine atoms in the solute molecule is linear. When the substituents are placed in positions 2 and 6 the steric hindrance is maximized and for two similar series (methyl esters of chlorobenzoic acids and chloroanisoles) the linear dependence can be written as

$$E_c = k_1 + k_2n \quad (6)$$

where k_1 and k_2 are constants and n is the number of substituents in the molecule.

For 2,6-substituted chloroanisoles ($n \geq 3$), $k_1 = 0$ and $k_2 = 0.36$ kcal/mole, the mean standard deviation being 0.23 kcal/mole. The corresponding values for the methyl esters of chlorobenzoic acids are -1.6 , 0.84 and 0.1 kcal/mole. The lack of data for esters, aldehydes and alcohols with $n \geq 3$ does not allow conclusions to be drawn for these classes of solutes. As a rule, the E_c values of solutes with $n \geq 3$ and having at least one substituent of large Van der Waals volume are positive because of steric hindrances.

ENTHALPIC SELECTIVITY OF POLAR STATIONARY PHASES

The calculation of the enthalpic selectivity (ΔH_s^0) for the non-polar stationary phase Apiezon L has already been discussed. To extend the column performance it is sometimes useful to apply polar stationary phases which can separate some isomeric solutes. The most convenient parameter for the evaluation of the enthalpic selectivity of polar stationary phases is the difference¹

$$\delta H_s^0 = \Delta H_s^{0p} - \Delta H_s^{0a} \quad (7)$$

where the superscripts a and p refer to non-polar and polar stationary phases, respectively. This difference allows one to discuss orientation forces in polar stationary phases and it is useful for identification.

We now discuss briefly the dependence of δH_s^0 on the solute properties. When comparing a polar stationary phase with a non-polar stationary phase, the following terms of eqn. 5 are changed: ΔH_{sc} , ΔH_h , and the numerical values of 0.7 and 0.6 n_{CH_3} for interaction with the polar stationary phase. Also, E_c disappears and is replaced by a new term related to the orientation forces. To avoid complicated calculations, homomorphous aromatic hydrocarbons are employed, and all the relative molar heats of solution will be related to these hydrocarbons as standards.

Taking into account these assumptions, we can write the following equation for ΔH_s^0 in a non-polar stationary phase (the homomorph is the standard)

$$\Delta H_s^{0*} = \Delta H_{scx} - \Delta H_{sch} + E_c - 0.6(n_{\text{CH}_3x} - n_{\text{CH}_3h}) \quad (8)$$

where the subscripts x and h refer to the polar solute and homomorphous standard, respectively. In a polar stationary phase, the relative molar heat of solution (the homomorph is the standard) is given by

$$\Delta H_s^{0*} = \Delta H_{scx} - \Delta H_{sch} - k(n_{\text{CH}_3x} - n_{\text{CH}_3h}) + \Delta O \quad (9)$$

where ΔO is the energy of the orientation forces. Assuming that the values of $\Delta H_{scx} - \Delta H_{sch}$ for the polar and non-polar stationary phases are similar and that $k \approx 0.6$, the difference between the relative molar heats of solution in the polar and non-polar stationary phases is as follows:

$$\delta H_s^{0*} = -E_c + \Delta O \quad (10)$$

In a more refined approach the difference between the dispersion forces in both stationary phases should be taken into account. The relative molar heats of solution for aromatic hydrocarbons (when benzene is taken as the standard) refer to the interaction of the substituent with the stationary phase; it is unlikely that the energy of the dispersion forces can be calculated from this value without knowing the heat of hole formation, ΔH_h . Therefore, it is more correct to use eqn. 10 and take into account the possible systematic error due to the differences in dispersion forces in the polar and non-polar stationary phases.

Table V lists experimental data on the relative heats of solution in PEGA (ΔH_s^0 , benzene is the standard) and the δH_s^{0*} (the homomorph is the standard) and δH_c^0 (standard is benzene) values. It can be seen that the orientation forces (ΔO) for chlorobenzene are negligibly small despite its large dipole moment. This may be explained by the differences between the molecular dipole and the microdipoles formed by atomic groups in the molecule. The orientation forces in GLC solutions appear between microdipoles of the stationary phase (C=O and C-O) and the solute microdipole C-Cl. The positive pole of the solute microdipole is strongly shielded by the chemically bound atoms, and, because of the the great mobility of π -electrons in the benzene ring, the positive pole is somewhat "spread" over the benzene ring. This "diffuseness" of the solute dipole prevents strong orientation forces with the more compact dipoles of the stationary phase.

The dipole moment of anisole is less than that of chlorobenzene, but the latter molecule has a diffuse microdipole while the former has one diffuse Ar-O dipole and one well defined O-CH₃ dipole. The O-CH₃ dipole has the same dimensions as the dipoles in the stationary phase and, therefore, ΔO of anisole is -0.7 kcal/mole. Methyl benzoate has four microdipoles, three of which (C=O, two C-O) can interact with the microdipoles of the stationary phase and one (C=O) which has a remarkable value; this is the cause of the great orientation interaction of methyl benzoate with PEGA: $\Delta O = -2.1$ kcal/mole. Although two solutes have formally the same C=O dipoles (methyl benzoate and benzaldehyde), the ΔO values may be different because of the different intramolecular shielding and electronic influences of the neighbouring atomic groups.

The main reason for the high ΔO value of benzyl alcohol is the energy of the hydrogen bond between the hydroxyl group of the alcohol and carbonyl oxygen of the stationary phase molecule: the dipole of the hydroxyl group is not large; therefore, the value $\Delta O = -5$ kcal/mole refers to the hydrogen bond.

When a second polar substituent is present in a *m*- or *p*-position the ΔO value decreases, but without additivity (Fig. 8). A lack of additivity in the dependence of ΔO on the number of polar substituents is due to steric hindrances when the microdipoles cannot be placed in solution in order to achieve the maximum orientation interaction.

Intramolecular influences on ΔO values can be observed by comparing the

TABLE V

SOME VALUES (KCAL/MOLE) OF THE PARAMETERS OF INTERACTION OF SOLUTES WITH POLYETHYLENE GLYCOL ADIPATE

Solute	$-\Delta H^\circ$	δH°	δH^{**}	ΔO
Toluene	0.86	0.16	—	—
<i>o</i> -Xylene	2.05	0.16	—	—
<i>m</i> -Xylene	1.82	0.35	—	—
<i>p</i> -Xylene	1.76	0.41	—	—
1,2,3-Trimethylbenzene	3.17	0.39	—	—
1,2,4-Trimethylbenzene	2.87	0.42	—	—
1,2,4,5-Tetramethylbenzene	3.93	0.61	—	—
Pentamethylbenzene	5.18	0.88	—	—
Hexamethylbenzene	6.58	1.03	—	—
<i>o</i> -Ethyltoluene	2.80	0.27	—	—
<i>m</i> -Ethyltoluene	2.51	0.48	—	—
<i>p</i> -Ethyltoluene	2.47	0.47	—	—
1,2-Diethylbenzene	3.37	0.64	—	—
1,3-Diethylbenzene	3.28	0.54	—	—
1,4-Diethylbenzene	3.24	0.76	—	—
1-Ethyl-4-isopropylbenzene	3.80	0.90	—	—
<i>p</i> -Isopropyltoluene	2.96	0.50	—	—
Chlorobenzene	1.30	—	0.35	-0.06
Anisole	2.65	—	-0.45	-0.72
Methyl benzoate	4.85	—	-0.25	-2.12
Benzaldehyde	4.45	—	-1.35	-3.02
Benzyl alcohol	6.32	—	-2.10	-5.02
<i>o</i> -Chloroanisole	4.90	—	-0.55	-0.88
<i>p</i> -Chloroanisole	4.45	—	-0.35	-0.81
2,4-Dichloroanisole	6.25	—	0.20	-1.37
2,5-Dichloroanisole	6.25	—	-0.15	-1.37
2,6-Dichloroanisole	4.70	—	-0.05	0.48
2,4,5-Trichloroanisole	7.15	—	-0.05	-0.55
2,4,6-Trichloroanisole	5.30	—	0.50	1.19
2,3,5,6-Tetrachloroanisole	6.40	—	1.45	1.72
Pentachloroanisole	7.80	—	1.40	2.03
Methyl <i>o</i> -chlorobenzoate	6.02	—	-0.45	-1.38
Methyl 2,4-dichlorobenzoate	6.85	—	0	-0.20
Methyl 2,5-dichlorobenzoate	6.90	—	0.05	-0.25
Methyl 2,3,6-trichlorobenzoate	7.80	—	-0.70	-0.59
Methyl <i>o</i> -toluate	5.65	—	-0.25	-1.92
Methyl <i>m</i> -toluate	5.75	—	-0.40	-2.45
Methyl <i>p</i> -toluate	5.75	—	-0.40	-2.49
Methyl 2,5-dimethylbenzoate	6.25	—	-0.25	-1.57
Methyl 3,4-dimethylbenzoate	6.55	—	0.05	-1.87
Methyl 2,4-dimethylbenzoate	6.25	—	-0.15	-1.52
Dimethyl phthalate	8.30	—	-0.65	-1.22
Dimethyl isophthalate	8.60	—	-0.90	-2.32
Dimethyl terephthalate	8.85	—	-0.30	-1.78
Dimethyl methylterephthalate	8.85	—	-0.30	-0.60
Methyl <i>p</i> -isopropylbenzoate	6.30	—	0.4	0.23
<i>o</i> -Methylbenzaldehyde	4.80	—	-0.75	-3.54
<i>m</i> -Methylbenzaldehyde	4.80	—	-0.70	-3.89
<i>p</i> -Methylbenzaldehyde	4.75	—	-0.60	-3.83

(Continued on p. 88)

TABLE V (continued)

Solute	$-\Delta H^\circ$	δH°	δH^{c*}	ΔO
2,5-Dimethylbenzaldehyde	5.40	—	-0.40	-2.03
2,4-Dimethylbenzaldehyde	5.55	—	-0.50	-2.13
<i>p</i> -Isopropylbenzaldehyde	5.90	—	-0.40	-0.30
1,2-Benzenedicarbaldehyde	6.75	—	-1.40	-2.96
1,4-Benzenedicarbaldehyde	6.80	—	-1.35	-3.30
<i>o</i> -Methylbenzyl alcohol	7.05	—	-2.75	-5.89
<i>m</i> -Methylbenzyl alcohol	7.00	—	-2.80	-6.18
<i>p</i> -Methylbenzyl alcohol	6.90	—	-2.70	-6.07
3,4-Dimethylbenzyl alcohol	7.50	—	-2.00	-1.90
2,4-Dimethylbenzyl alcohol	7.65	—	-2.00	-1.74
2,5-Dimethylbenzyl alcohol	7.65	—	-2.00	-1.69
<i>p</i> -Isopropylbenzyl alcohol	7.65	—	-1.75	-2.25
<i>p</i> -Cresyl acetate	6.00	—	-1.30	-1.57
<i>o</i> -Tolyl acetate	6.80	—	-1.10	-0.27
<i>p</i> -Tolyl acetate	6.75	—	-0.80	-0.42
2,4-Dimethylbenzyl acetate	7.35	—	-0.40	-0.14
2,5-Dimethylbenzyl acetate	7.25	—	-0.35	-0.04
3,4-Dimethylbenzyl acetate	7.60	—	-0.50	-0.40

data for *o*-isomers with those for *m*- and *p*-isomers. The orientation forces for *o*-isomers are usually 0.1–0.6 kcal/mole less than those of *m*- and *p*-isomers. Proximity of the substituents (*o*-isomers) leads to increasing steric hindrance to the optimum interaction of each polar solute group with the polar groups of the stationary phase.

Orientation forces depend also on the sign of the mesomeric effect for the second substituent. For example, 1,4-benzenedicarbaldehyde has two strong polar groups each having a negative mesomeric effect and the ΔO value for this solute is -3.3 kcal/mole; *p*-methylbenzaldehyde has one carbonyl group and one methyl group (the latter with a positive mesomeric effect) and the ΔO value for this solute is -3.8 kcal/mole. Thus, with the introduction of a second substituent having a small dipole but a mesomeric effect of different sign, the orientation forces increase as compared with the dicarbaldehyde.

Since the orientation forces and the concentration effect are both proportional to the dipole moments of the microdipoles and their number in the solute molecule, E_c and ΔO are correlated with each other (Fig. 9). The mean standard deviation for this correlation is 0.4 kcal/mole, which is poor for quantitative calculations. However, the qualitative relation between these effects is clear. The difference between the concentration effect and the orientation forces is due to the fact that the former occurs between homogeneous solute molecules while the latter appear between solute molecules and the stationary phase microdipoles.

The ΔO values are useful for understanding the intermolecular interaction in solutions. However, δH_s° values calculated from the relative molar heats of solution can be employed for identification in a more simple manner. The dependence of δH_s° on the number of substituents for different solutes is shown in Fig. 10. The data show the differences between monosubstituted benzenes: thus, esters, ethers, aldehydes and alcohols are clearly distinguished by more than 0.2 kcal/mole. For disubstituted benzene derivatives one can see that alcohols have the lowest δH_s° values, and those are *ca.* 1 kcal/mole less than those of aldehydes and esters. Disubstituted

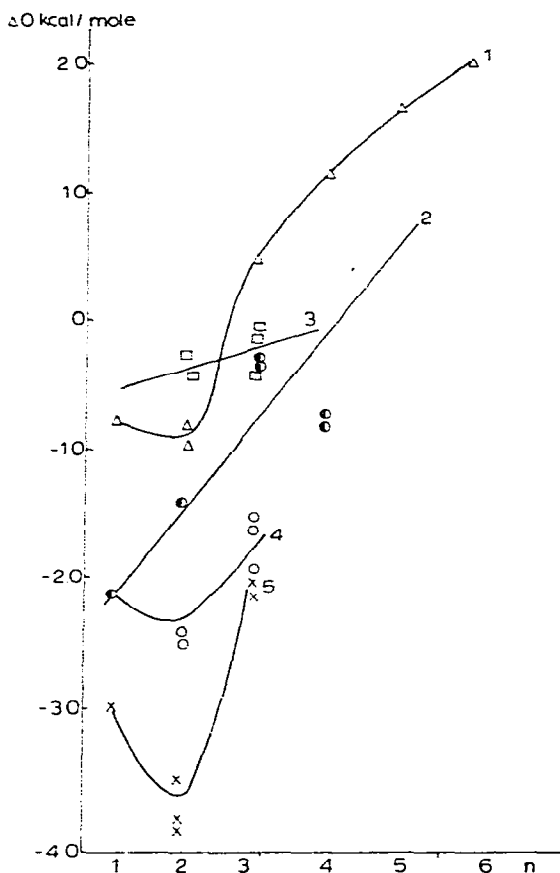


Fig. 8. Dependence of ΔH° on the number of substituents in the solute molecules. 1 = Chloroanisoles; 2 = methyl chlorobenzoates; 3 = acetates; 4 = methyl methylbenzoates; 5 = methyl aldehydes.

derivatives having a methyl group and an ester, aldehydes or acetate group differ in their δH_s° value by *ca.* 0.2 kcal/mole. Methyl esters of dicarboxylic acids differ markedly in δH_s° from methyl-substituted derivatives. No marked differences are observed between chloro- and methyl-substituted benzene derivatives. The δH_s° differences for polysubstituted benzene derivatives seem to be insignificant.

SELECTIVITY OF DIFFERENT STATIONARY PHASES

The relative retention data of the solutes in four different stationary phases (naphthalene is the standard) are listed in Table VI. Two of the stationary phases are structure-selective [silicone OV-17 with 50% of phenyl groups, and 5-ring poly(phenyl ether)] because of the presence many phenyl rings; the two remaining phases are non-polar and polar liquids respectively. The relative retention data show selectivity at 150° C, and the relative molar heats of solution indicate temperature influences on selectivity.

Because the main chromatographic interest is the resolution of isomeric substances, let us consider the differences in the resolution using these stationary phases.

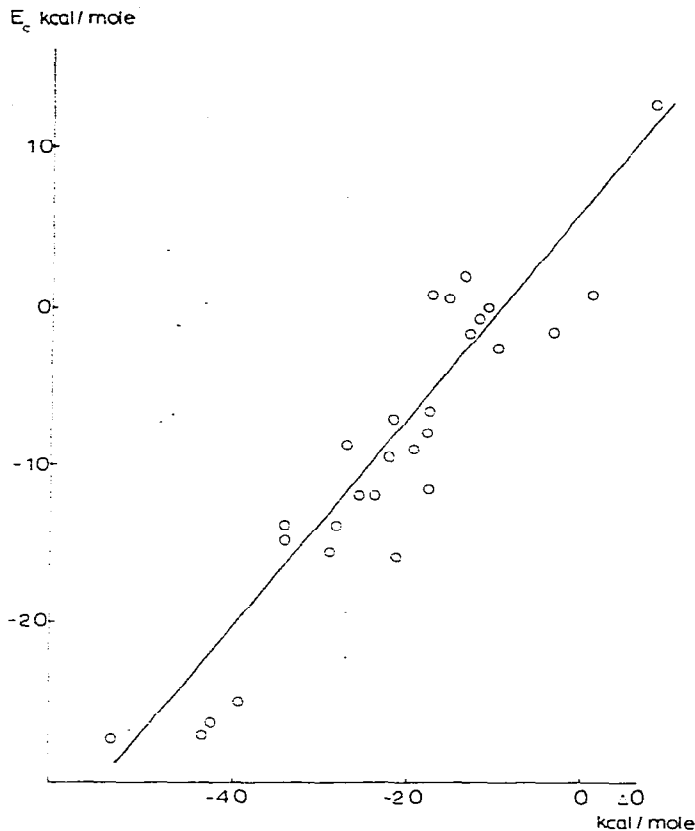


Fig. 9. Correlation between E_c and ΔO .

Some pairs of poorly separated or unresolved isomers are given in Table VI. *o*- and *p*-toluic alcohols have very close retentions on OV-17 and Apiezon L, while these solutes may be separated on poly(phenyl ether). Using the ether stationary phase, it is observed that when the column temperature decreases the relative retention of these isomers increases. Another pair of poorly separated solutes is 2,4- and 2,5-dimethylbenzyl alcohols: at 150° C they are not separated on any stationary phase, and the molar heats of solution are the same on all the stationary phases. It is concluded that their separation would be difficult to achieve at any column temperature. The pair *o*- and *m*-methylbenzaldehyde are not resolved. Some pairs, which are not resolved on OV-17, are separated on other stationary phases, *e.g.*, *o*- and *p*-tolylacetates, terephthalaldehyde and phthalaldehyde and methyl esters of 2,5- and 2,4-dimethylbenzoic acid.

It should be noted that OV-17 and poly(phenyl ether) have no specific resolving power as compared with non-polar or polar stationary phases. This may be explained by the presence of the benzene ring in the solute: a stationary phase containing a large number of benzene rings is sensitive mainly to the benzene ring of the solute and not to the positions of the substituents.

TABLE VI

RELATIVE RETENTION DATA ON DIFFERENT STATIONARY PHASES
Naphthalene is the standard.

Solute	OV-17		Poly(phenyl-ether)		Apiezon L		PEGA	
	ΔH_2^0 (kcal/ mole)	<i>r</i>	ΔH_2^0 (kcal/ mole)	<i>r</i>	ΔH_2^0 (kcal/ mole)	<i>r</i>	ΔH_2^0 (kcal/ mole)	<i>r</i>
Benzyl alcohol	0.32	0.57	0.18	0.60	0.66	0.32	-1.37	1.39
<i>p</i> -Toluic alcohol	-0.62	0.74	-0.67	0.83	0.70	0.54	-1.96	2.02
<i>m</i> -Toluic alcohol	-0.62	0.75	-0.79	0.86	0.71	0.53	-2.06	2.07
<i>o</i> -Toluic alcohol	-0.46	0.81	-0.74	0.91	0.60	0.59	-2.09	2.27
2,4-Dimethylbenzyl alcohol	-1.12	1.30	-1.4	1.53	-0.66	0.97	-2.71	3.23
2,5-Dimethylbenzyl alcohol	-1.14	1.31	-1.43	1.54	-0.66	0.97	-2.72	3.20
3,4-Dimethylbenzyl alcohol	-1.32	1.37	-1.55	1.70	-0.54	1.06	-2.57	3.69
Cuminol	-1.54	1.57	-1.62	1.76	-0.50	0.76	-0.73	1.30
<i>p</i> -Cresyl acetate	-0.84	0.80	-0.84	0.80	0.20	0.50	-1.04	0.97
Benzyl acetate	-0.84	0.82	—	—	—	—	—	—
<i>o</i> -Tolyl acetate	-1.61	1.39	-1.74	1.44	-0.81	0.89	-1.86	1.57
<i>p</i> -Tolyl acetate	—	—	-1.72	1.43	-0.95	0.91	-1.80	1.52
2,4-Dimethylbenzyl acetate	-2.26	2.30	-2.50	2.45	-1.96	1.62	-2.39	2.36
2,5-Dimethylbenzyl acetate	-2.14	2.19	-2.46	2.31	-1.92	1.51	-2.32	2.20
3,4-Dimethylbenzyl acetate	-2.63	2.70	-2.60	2.87	-2.09	1.83	-2.64	2.80
Benzaldehyde	0.66	0.30	0.57	0.30	1.18	0.20	0.52	0.43
<i>m</i> -Methylbenzaldehyde	0.29	0.53	0.32	0.56	0.80	0.38	0.16	0.68
<i>p</i> -Methylbenzaldehyde	0.22	0.58	0.31	0.61	0.75	0.40	0.27	0.76
<i>o</i> -Methylbenzaldehyde	0.30	0.54	0.25	0.55	0.75	0.39	0.17	0.67
2,4-Dimethylbenzaldehyde	-0.46	0.99	-0.40	1.06	-0.12	0.80	-0.59	1.13
2,5-Dimethylbenzaldehyde	-0.44	0.92	-0.41	0.99	-0.10	0.74	-0.45	1.03
3,4-Dimethylbenzaldehyde	-1.12	1.21	-1.08	1.35	-0.50	0.97	-0.94	1.28
<i>p</i> -Isopropylbenzaldehyde	—	—	-1.12	1.29	-0.47	0.91	-0.60	1.41
Terephthalaldehyde	-2.06	1.77	-1.70	2.38	-0.46	0.92	-1.85	4.35
Phthalaldehyde	-2.12	1.78	-1.73	2.51	-0.36	0.98	-1.82	4.45
Methyl benzoate	0.1	0.58	-0.05	0.55	0.29	0.51	0.10	0.63
Methyl <i>o</i> -toluate	-0.06	0.85	-0.56	0.81	-0.50	0.65	-0.69	0.84
Methyl <i>m</i> -toluate	-0.72	1.0	-0.72	0.98	-0.42	0.76	-0.80	1.02
Methyl <i>p</i> -toluate	-0.70	1.04	-0.86	1.04	-0.42	0.80	-0.79	1.06
Methyl 2,5-dimethylbenzoate	-1.38	1.43	-1.25	1.41	-1.11	1.17	-1.30	1.03
Methyl 2,4-dimethylbenzoate	-1.47	1.51	-1.32	1.50	-1.17	1.24	-1.30	1.03
Methyl 3,4-dimethylbenzoate	-2.16	2.19	-2.10	2.31	-1.72	1.72	-1.58	2.15
Methyl <i>p</i> -isopropylbenzoate	-2.16	2.17	-2.07	2.20	-1.69	1.82	-1.36	1.79
Dimethyl phthalate	—	—	-3.60	5.85	-1.96	2.06	-3.61	8.53
Dimethyl terephthalate	—	—	-3.82	7.10	-2.65	3.35	-3.36	7.77
Dimethyl isophthalate	—	—	-4.05	7.75	-2.70	3.43	-3.67	8.79
Dimethyl methylterephthalate	—	—	-4.64	10.3	-3.53	5.28	-3.92	10.7

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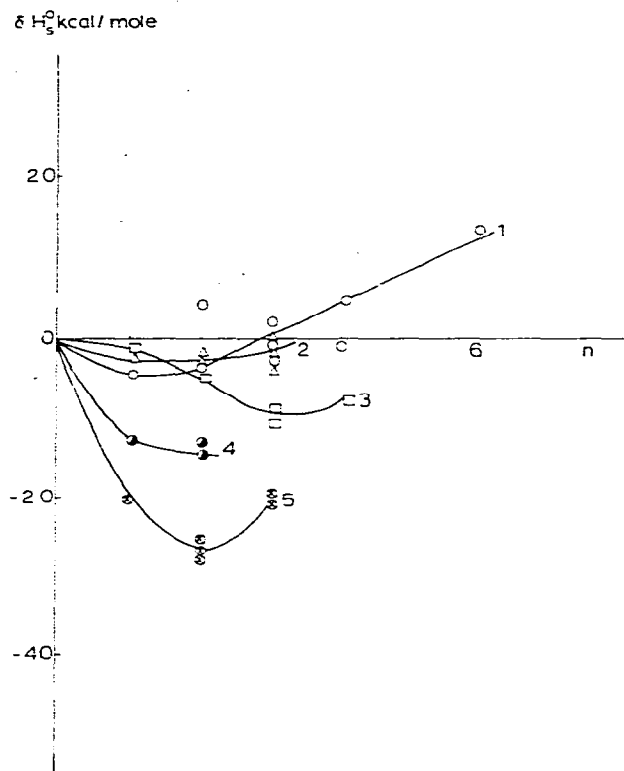


Fig. 10. Variation of δH_f° with the number of substituents in the solute molecules. 1 = Chloroanisoles; 2 = methyl methylbenzoates; 3 = methyl chlorobenzoates; 4 = polyaldehydes; 5 = alcohols.

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