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GAS-LIQUID CHROMATOGRAPHY OF DISUBSTITUTED BENZENE ISOMERS

I. SEPARATION AND STUDY OF THE DICHLOROBENZENES

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SUMMARY

Dichlorobenzene isomers were separated on squalane, silicone oil, polyethyleneglycol, polyoxyethylenesorbitan monostearate and polyethyleneglycol succinate. Types of interactions and forces which affected the specific retention volumes and elution orders were discussed. Thermodynamic quantities were calculated and studied on squalane and polyethyleneglycol. Polyesters were selective for the separation of these isomers.

INTRODUCTION

Dichlorobenzenes were studied by COWAN AND HARTWELL[1] on Bentone 34, MORTIMER AND GENT[2] on Bentone 34 modified with silicone oil, and HABBOUSH AND NORMAN[3] on Apiezon L, dinonyl phthalate, polyethyleneglycol–stearic acid, tritolyl phosphate, 2,4,7-trinitrofluorenone and silicone gum rubber. The mechanism of separations was not available. LANGER AND PURNELL[4] calculated thermodynamic quantities for dichlorobenzenes on benzyl diphenyl and 7,8-benzquinoline.

In the present work, quantitative separations for dichlorobenzene isomers were studied on squalane (SQ), silicone oil (SO), polyethyleneglycol 1500 (PEG), polyethyleneglycol succinate (PEGS) and polyoxyethylenesorbitan monostearate (PA). The specific retention volumes, separation factors and fractional band impurities were calculated. The solute–solvent interactions affecting the retention volumes and elution orders were discussed. Thermodynamic quantities were also calculated and discussed on SQ and PEG.

EXPERIMENTAL AND RESULTS

Apparatus

A Perkin–Elmer Model 451 Fractometer equipped with a thermistor-type thermal conductivity detector was used. The recorder was a 2.5 mV Honeywell Brown

TABLE I

THE CHEMICAL COMPOSITION OF THE LIQUID PHASES USED[a]

Chemical Name	*Formula*	*D*[b]	*Mol. wt.*	*MOT*[c] *(°C)*
Polyethyleneglycol (PEG)	$(CH_2)_4(OH)_2O(OCH_2CH_2)_n$	1.152	1500	225
Polyethyleneglycol succinate (PEGS)	$[O(CH_2CH_2O)_2COCH_2CH_2CO\text{-}]_n$	—	$(188.2)_n$	225
Polyoxyethylenesorbitan monostearate (PA)	—	—	—	160
2,6,10,15,19,23-Hexamethyltetracosane (squalane) (SQ)	$C_{30}H_{62}$	0.829	422.5	160
Silicone oil (MS 200/50) (SO)	$(CH_3)_3Si\text{-}[OSi(CH_3)_2]n\text{-}O\text{-}Si(CH_3)_3$	0.971	—	200

[a] G. W. HINE, Perkin–Elmer Ltd., Beaconsfield, Bucks, Great Britain, private communication.

[b] Density at 20° in g/ml.

[c] Maximum operating temperature when columns were packed.

Electronic unit. Nitrogen was used as the carrier gas. The average column temperature was controlled to within ± 0.2°. Columns were specially ordered from Perkin–Elmer, Great Britain. They were stainless-steel tubing (2 m long and ¼ in. O.D.) bent into a U-shape and surrounded by asbestos sleeves to ensure uniform heating. The chemical composition of the liquid phases used is shown in Table I. Packing specifications of all columns used were identical. The weight of pure liquid phase per column was 3.40 g and the liquid on the support was 20% (w/w). These were certified in this laboratory using a solvent extraction technique. The solid support was 60–80 mesh Chromosorb P.

TABLE II

SPECIFIC RETENTION VOLUMES, V_g^0 (ml/g), FOR DICHLOROBENZENE ISOMERS ON DIFFERENT LIQUID PHASES AND AT DIFFERENT COLUMN TEMPERATURES

Phase	*Temp. (°C)*	*Dichlorobenzene isomer*		
		Ortho	*Meta*	*Para*
PEGS	80	662	450	511
	100	335	233	264
	120	184	132	147
	180	59.0	46.0	50.0
PA	100	303	212	235
	120	174	124	136
SO	120	397	345	345
	140	257	226	226
	180	107	95.0	95.0
SQ	120	412	294	320
	130	297	214	233
	140	225	163	176
PEG (1500)	100	88.0	75.1	75.1
	120	57.8	50.8	50.8
	140	40.5	35.7	35.7
	160	31.0	27.0	27.0

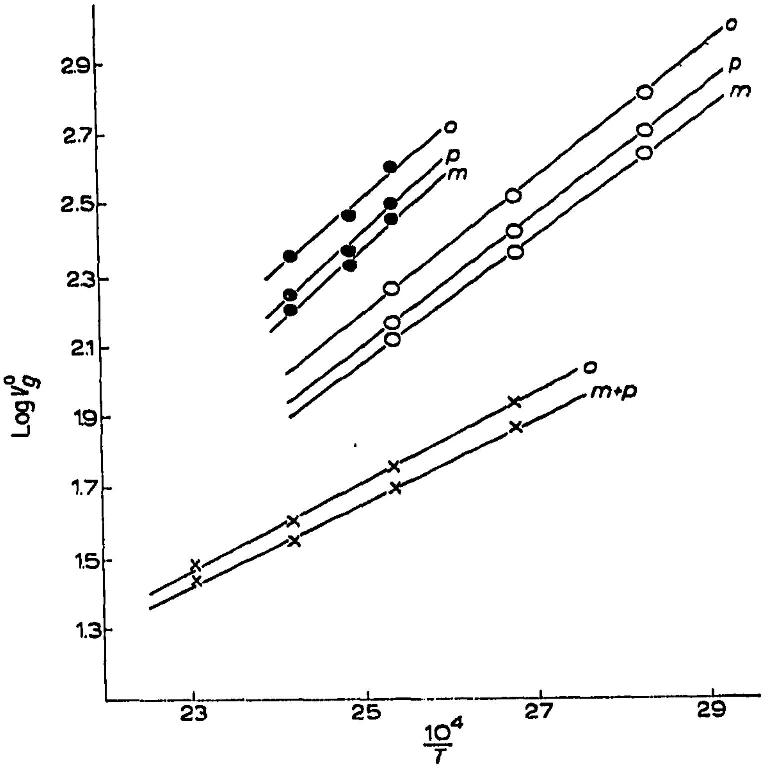

Fig. 1. Variation of log V_g^0 with $1/T$ for dichlorobenzene isomers on the following liquid phases: ●, squalane; ○, polyethyleneglycol succinate; ×, polyethyleneglycol.

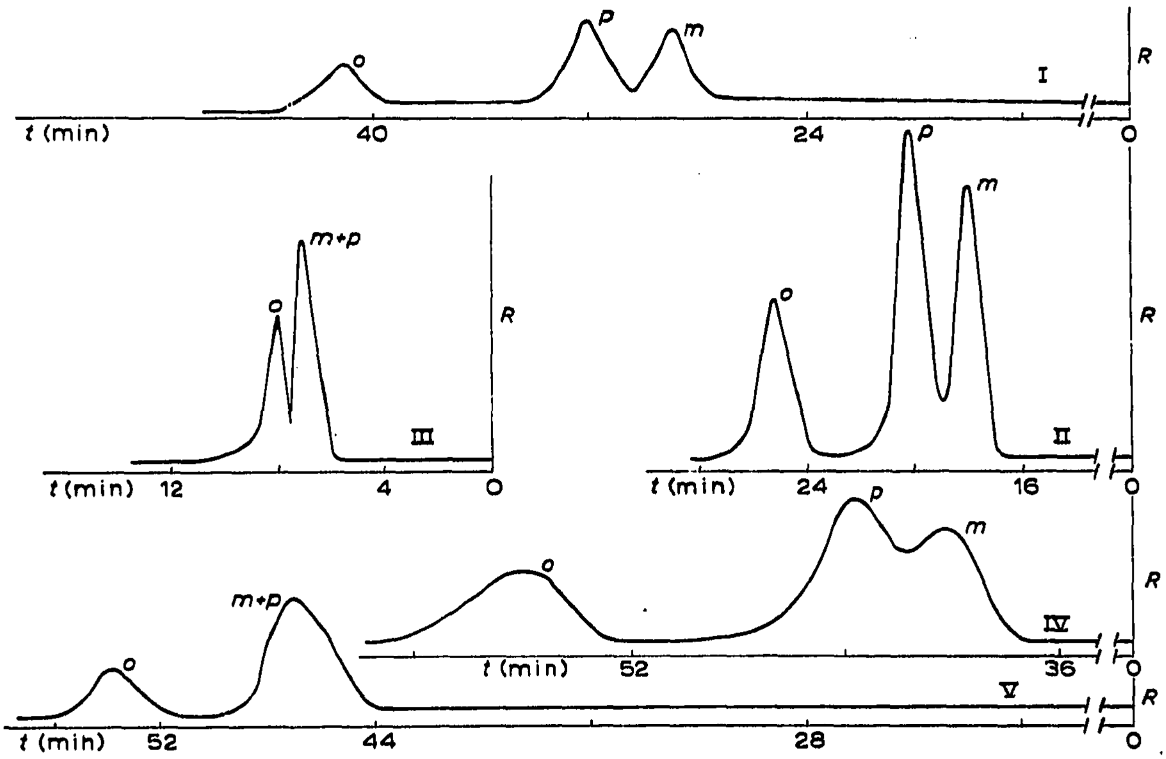

Fig. 2. Chromatograms showing the separation of dichlorobenzene isomers at 120° on: (I) PA; (II) PEGS; (III) PEG; (IV) SQ; and (V) SO. t is the time in minutes and R is the recorder deflection.

Materials

Pure *o*-, *m*-, and *p*-dichlorobenzenes were obtained from Hopkin and Williams Ltd., Great Britain.

Sampling

Equal weights of the isomers were blended in a cylindrical Pyrex cell, having a 3 ml capacity, made in this laboratory. Sample sizes ranged from 0.5 to 1 μl. The injections were made using a 10-μl Hamilton 1-in. fixed needle syringe. An optimum flow rate of 20 ml/min at NTP was encountered throughout the investigations. The average inlet pressure was 6 ± 1 p.s.i. The outlet pressure was atmospheric.

The specific retention volumes, $V_g{}^0$, were calculated following the well-known procedure given by LITTLEWOOD *et al.*[5]. The retention volume for the air peak was taken to be zero. Specific retention volumes for dichlorobenzene isomers at different column temperatures on the liquid phases examined are listed in Table II.

Variation of log $V_g{}^0$ with $1/T$ is linear (see Fig. 1). Fig. 2 shows the separation of dichlorobenzenes on the liquid phases examined.

The number of theoretical plates, *n*, was calculated as recommended by JOHNSON AND STROSS[6]. Table III gives the number of theoretical plates, separation factors and fractional band impurities for the isomers.

Electron polarizabilities per unit volume, α_e^v, were calculated using the Clausius–Mosotti equation:

$$\alpha_e^v = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{3}{4\pi N} \qquad (1)$$

where *n* is the refractive index and *N* is the Avogadro number. Refractive indices of

TABLE III

NUMBER OF THEORETICAL PLATES, *n*, SEPARATION FACTORS, α, AND FRACTIONAL BAND IMPURITIES, η, FOR DICHLOROBENZENES ON DIFFERENT LIQUID PHASES AND COLUMN TEMPERATURES[a]

Dichlorobenzene isomer	*Phase (°C)*	*n*	*α*	*η*
Meta	PEGS	1860		
Para	(80°)	1860	1.14	$2 \cdot 10^{-3}$
Ortho		2000	1.29	$5 \cdot 10^{-8}$
Meta	PA	2100		
Para	(100°)	2930	1.11	$4 \cdot 10^{-3}$
Ortho		2470	1.29	$1 \cdot 10^{-12}$
Meta	PEG	475	1.0	
Para	(100°)	475		
Ortho		550	1.17	$5 \cdot 10^{-2}$
Meta	SO	3220		
Para	(120°)	3220	1.0	
Ortho		4250	1.15	$3 \cdot 10^{-6}$
Meta	SQ	752		
Para	(120°)	890	1.08	$1 \cdot 10^{-1}$
Ortho		1088	1.28	$5 \cdot 10^{-5}$

[a] Where a set of isomers was examined at more than one temperature, values of *n*, α, and η are recorded for the temperature at which resolution was more satisfactory.

TABLE IV

DIPOLE MOMENTS, REFRACTIVE INDICES, ELECTRON POLARIZABILITIES AND BOILING POINTS OF DICHLOROBENZENE ISOMERS

Dichlorobenzene isomer	*D*	$n_D^{55°}$	*E. P.* $(cm^3 \times 10^{26})$	*B. P.* (°C)
Ortho	2.69	1.5335	12.306	179
Meta	1.55	1.5288	12.215	173
Para	0.0	1.5305	12.248	173

dichlorobenzene isomers at 55° were measured in this laboratory using an Ape refractometer.

Dipole moments were calculated as given by SMITH[7]. Dipole moments and other physical constants are tabulated in Table IV.

The activity coefficients at infinite dilution, γ_2^0, were calculated on SQ and PEG from the following equation[8]:

$$\gamma_2^0 = \frac{17.04 \times 10^6}{M_1 \cdot P^0 \cdot V_g^0} \tag{2}$$

γ_2^0 measures the non-ideal behavior in both the gas phase and solution. Activity coefficients for dichlorobenzenes on SO, PEGS and PA could not be determined due to their undetermined molecular weights (M_1). Table V gives data on vapor pressures and activity coefficients.

The excess partial molar free energy, $\Delta\bar{G}_e^0$, the partial molar excess entropy, $\Delta\bar{S}_e^0$, and the partial molar excess enthalpy $\Delta\bar{H}_e^0$, of mixing at infinite dilutions were calculated as given by LANGER AND PURNELL[4]. These data are shown in Table VI.

Dichlorobenzene isomers were selectively resolved on PEGS and PA (as shown in Table III and Fig. 2). SO and PEG failed to resolve *m*- and *p*-isomers.

TABLE V

VAPOR PRESSURES[a], *P* (mm Hg), AND ACTIVITY COEFFICIENTS AT VARIOUS TEMPERATURES

Data	*Temp.* (°C)	*Dichlorobenzene isomer*		
		Ortho	*Meta*	*Para*
Vapor pressure	100	62.55	81.20	77.70
	110	91.57	117.4	112.6
	120	130.9	165.7	159.3
	130	183.1	229.2	220.9
	140	251.0	311.0	300.4
Activity coefficient γ_2^0 (on PEG)	100	2.064	1.863	1.947
	120	1.501	1.349	1.404
	140	1.117	1.023	1.059
Activity coefficient γ_2^0 (on SQ)	120	0.748	0.828	0.791
	130	0.742	0.822	0.784
	140	0.714	0.796	0.763

[a] These were calculated using Antoine's equations and constants (see ref. 9).

TABLE VI

THERMODYNAMIC DATA ON DIFFERENT PHASES

Phase	*Dichlorobenzene isomer*	*Temp. (°C)*	*Thermodynamic data*		
			$\Delta \bar{G}_e^0$ *(cal/mole)*	$\Delta \bar{H}_e^0$ *(kcal/mole)*	$\Delta \bar{S}_e^0$ *e.u.*
PEG	*ortho*	100	536.6		
		120	317.1	3.870	+9.040
		140	90.6		
	meta	100	460.7		
		120	233.7	3.933	+9.414
		140	18.5		
	para	100	493.3		
		120	264.2	4.007	+9.524
		140	47.1		
SQ	*ortho*	120	−226.8	−0.530	−0.771
		130	−239.2		
		140	−276.2		
	meta	120	−147.4	−0.552	−1.030
		130	−156.6		
		140	−187.5		
	para	120	−183.1	−0.485	−0.768
		130	−195.1		
		140	−222.1		

DISCUSSION

The different values of activity coefficients, γ_2^0, of Table V could be explained using the two terms, $\Delta \bar{H}_e^0$ and $\Delta \bar{S}_e^0$, of the following equation[8]:

$$\ln \gamma_2^0 = \frac{\Delta \bar{H}_e^0}{RT} - \frac{\Delta \bar{S}_e^0}{R} \tag{3}$$

$\Delta \bar{H}_e^0$ is related to the disparities in the intermolecular forces and $\Delta \bar{S}_e^0$ to the inequalities in the volumes of solute and solvent molecules. The following approximation is also valid:

$$\Delta \bar{H}_e^0 \doteqdot z\Delta W = z\left(\tfrac{1}{2}W_{11} + \tfrac{1}{2}W_{22} - W_{12}\right) \tag{4}$$

where z is the number of nearest neighbors, ΔW the molar interaction change energy, and W_{11}, W_{22}, W_{12} are the pairwise potential energies of interaction, respectively, for two solvent molecules, two solute molecules and between a solute and a solvent molecule.

The inequalities in the volumes of solute and solvent molecules means that the "packing" of molecules of different sizes is less orderly. It appears that in PEG, W_{11} and W_{22} are higher than W_{12}. This might be due to internal association through intermolecular hydrogen bonding that such a relatively polar phase may exert. This would lead to a higher value of $\Delta \bar{H}_e^0$ and consequently to a higher value of γ_2^0. Although the $\Delta \bar{S}_e^0$ term may give a large contribution, the overall value results in a higher value than unity for γ_2^0 and leads to a positive deviation from Raoult's law.

In SQ, which is not polar, solvent–solvent interaction is much weaker than in PEG. The W_{12} contribution might be small due to the induction or London forces.

Moreover, SQ which has a branched methyl group in its structure, may give a small positive contribution to the partial excess entropy term. This might explain the lower than unity values of $\gamma_2{}^0$ which would yield a negative deviation from Raoult's law. The values of $\gamma_2{}^0$ and $\Delta\bar{H}_e{}^0$ in PEG and SQ are in agreement with the above argument.

Any interaction in GLC has to be associated with interaction energy and entropy (configurational) requirements. Each one of these factors would predominate, if it has a larger value than the other, and characterize the overall interaction. Table VI shows that the difference between $\Delta\bar{S}_e{}^0$ and $\Delta\bar{H}_e{}^0$ values for *m*- and *p*-isomers in PEG are not large enough to cause one of the parameters to predominate and cause separation, while in SQ, although the $\Delta\bar{H}_e{}^0$ values of the *m*-isomer are higher than that of the *p*-isomer, it is associated with a higher entropy requirement which would predominate and cause the *m*-isomer to be eluted before the *p*-isomer.

The calculation of thermodynamic quantities are susceptible to many errors[4] especially in the calculations of $\Delta\bar{G}_e{}^0$ and $\Delta\bar{H}_e{}^0$, and hence $\Delta\bar{S}_e{}^0$. The calculated thermodynamic quantities for the present work are good as far as they have been used for comparison.

The observed order of elution of the isomers was *meta-*, *para-* and then *ortho*. This is in disagreement with the order of calculated dipole moments of the isomers (see Table IV). *p*-Dichlorobenzene may undergo polarization by the influence of the dipoles or the induced dipoles of the stationary phase. The values of electron polarizabilities support the above mechanism. Therefore, the order of elution of dichlorobenzene isomers follows their order of increasing electron polarizabilities.

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