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Solvation in weak complexing *n*-octyl phthalate and *n*-octyl tetrachlorophthalate solvents by gas chromatography

Gyungse Park^a, Colin F. Poole^{a,b,*}

^aDepartment of Chemistry, Wayne State University, Detroit, MI 48202, USA

^bZeneca/Smithkline Beecham Centre for Analytical Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AY, UK

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Abstract

The solution properties of a varied group of solutes in di-*n*-octyl phthalate and di-*n*-octyl tetrachlorophthalate over the temperature range 60 to 120°C were studied by gas chromatography. The solvation parameter model was used to assign the contribution of individual intermolecular interactions to the gas–liquid partition coefficients. The dominant interaction was dispersion with only small contributions from dipole-type interactions, *n*- and π -electron donor/acceptor interactions (for the tetrachlorophthalate ester only), and solvent hydrogen-bond base interactions. Neither phthalate ester exhibited solvent hydrogen-bond acid properties. Complexes formed between solutes and these phthalate ester solvents are likely to be of the Van der Waals type, perhaps augmented by dipole-type interactions and hydrogen-bond complexation with hydrogen-bond acid solutes. In addition, *n*- and π -electron complexation interactions, in the temperature range studied, may contribute to complex formation with the tetrachlorophthalate ester, but are too weak to be the dominant interactions involved. In general, the range of chromatographic selectivity obtainable through exploitation of the phthalate and tetrachlorophthalate nucleus does not warrant their selection as building blocks for new polymer-supported phases with the expectation of providing opportunities to extend the selectivity range of existing gas chromatographic stationary phases. In addition, the influence of interfacial adsorption as a retention mechanism for the determination of solvent properties and as a potential source of disagreement between reported solvent properties for the phthalate esters is discussed.

Keywords: Interfacial adsorption; Retention mechanisms; Solvation parameter model; Di-*n*-octyl phthalate; Di-*n*-octyl tetrachlorophthalate

1. Introduction

The dialkyl phthalates are moderately polar solvents with a capacity for selective hydrogen-bond

base interactions through the oxygen atoms of the ester group as well as participating in charge transfer interactions through the electron acceptor capacity of the aromatic ring [1–3]. The introduction of electronegative substituents on the aromatic ring, as for example in dialkyl tetrachlorophthalates, enhances the capacity of the aromatic ring to function as an electron acceptor. The dialkyl tetrachlorophthalates have been used as stationary phases in gas–liquid

* Corresponding author. Address for correspondence: Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AY, UK.

chromatography to affect separations based on these principles, and in particular, for the separation of aromatic compounds and olefins from their saturated analogs and for the separation of positional and geometric isomers such as *m*- and *p*-xylene [4–7]. Cadogan and Purnell [8] and Langer et al. [9,10] used gas chromatography to determine the formation constants for charge transfer complexes between dialkyl tetrachlorophthalates and aromatic compounds in solvents such as squalane. The tetrachlorophthalates were characterized as forming weak complexes with aromatic compounds consistent with steric hindrance, in which overlap of the aromatic rings is impeded by the out-of-plane ester groups of the phthalate. The evidence for this being the low entropy of complex formation. Eon et al. [11,12] determined the formation constants for furan, thiophene, pyrrole and some other solutes with di-*n*-butyl tetrachlorophthalate by gas chromatography indicating the formation of strongly bound complexes. A detailed review of complexation in chromatography, including studies of the dialkyl phthalate esters is provided by de Ligny [13]. In addition, Langer [14] described the preparation of several novel phases consisting of tetrachlorophthaloyl oligomers, as an approach for increasing the concentration of the selective tetrachlorophthaloyl group compared to the dialkyl tetrachlorophthalate group in phases with higher maximum operating temperature limits.

The cornerstone of the above-mentioned studies was the tacit assumption that the selectivity of the phthalate phases was a function of their capacity to act as electron acceptors in the formation of charge transfer complexes. On the one hand there is ample evidence that the dialkyl phthalates can form complexes from spectroscopy and synthesis [13,15], but the mechanistic argument that this results primarily from charge transfer complexation is less compelling. On the other hand, a comprehensive survey of the solvation properties of common stationary phases [16–18] did not reveal any phases that exhibited a significant capacity for π - and *n*-electron acceptor interactions. Therefore, if it could be demonstrated that these interactions were significant for the dialkyl phthalates, it would suggest obvious targets for the design of modern stationary phases, incorporating electron acceptor sites in their structure with more

favorable properties for column preparation and high temperature operation combined with the expectation of extending the range of selective stationary phases currently available. These factors and the fact that the dialkyl phthalates are important industrial chemicals in their own right, and therefore their solvation characteristics are of general interest, prompted this study.

Retention in gas–liquid chromatography can be a complex process involving partitioning with the liquid stationary phase and interfacial adsorption at the support surface and/or liquid surface [1,18–20]. This can be expressed as

$$V_N^* = V_L K_L + A_{GL} K_{GL} + A_{LS} K_{GLS} \quad (1)$$

where V_N^* is the net retention volume per gram of column-packing, V_L the volume of liquid stationary phase per gram of column-packing, K_L the gas–liquid partition coefficient, A_{GL} the gas–liquid interfacial area per gram of column-packing, K_{GL} the adsorption coefficient at the gas–liquid interface, A_{LS} the liquid–solid interfacial area per gram of column-packing, and K_{GLS} the coefficient for adsorption at the liquid–solid interface. In applying Eq. 1 to retention data it is assumed that the individual retention mechanisms are independent and additive, the solute concentration is in a region of the isotherm where infinite dilution and/or zero surface coverage approximations apply, and the contribution to retention from the structured liquid phase layer in close contact with the support surface can be neglected. These conditions are met by the data to be reported in this paper. Division of both sides of Eq. 1 by V_L allows the gas–liquid partition coefficient to be evaluated independently of the other contributions to retention, by extrapolation of the experimental data to obtain the intercept on the V_N^*/V_L axis, corresponding to an infinite liquid phase volume. In theory, it should be possible to determine the adsorption coefficients in Eq. 1 from a knowledge of the surface area terms A_{GL} and A_{LS} ; in practice this is difficult to do due to the lack of a straightforward and reliable experimental method for determining surface areas as a function of the liquid phase loading [19]. Insights into the importance of adsorption as a retention mechanism, however, may be obtained by comparing the observed experimental

retention with the value calculated, assuming that the only contribution to retention was from gas–liquid partitioning [19,21,22].

The most generally useful model to characterize the individual contributions from fundamental intermolecular interactions to the gas–liquid partition coefficient is the solvation parameter model developed by Abraham and co-workers [23–25] and exploited in the same or modified form by Poole and co-workers [16–18,26,27], by Carr [28] and by Li and Carr [29] to establish the solvent properties of a wide range of common stationary phases. The basis of these models is the cavity model of solvation, in which the transfer of a solute from the gas phase to solution in the stationary phase is considered to occur in three stages: (1) the creation of a cavity in the solvent of a suitable size to accommodate the solute, (2) reorganization of the solvent molecules around the cavity and (3) introduction of the solute into the cavity where it is able to interact with the surrounding solvent molecules. The solvation parameter model provides the following general equation relating the gas–liquid partition coefficient, K_L , to the characteristic interactions for the solvation process

$$\log K_L = c + rR_2 + s\pi_2^H + a\alpha_2^H + b\beta_2^H + l \log L^{16} \quad (2)$$

where c is a constant, R_2 the solute excess molar refraction, π_2^H the effective solute dipolarity/polarizability, α_2^H the effective solute hydrogen-bond acidity, β_2^H the effective solute hydrogen-bond basicity and L^{16} the solute gas–liquid partition coefficient on *n*-hexadecane at 25°C. The explanatory variables (R_2 , π_2^H , α_2^H , β_2^H and $\log L^{16}$) are solvation parameters derived from equilibrium measurements and are free energy related terms characteristic of the monomeric solute. Values of the solvation parameters for more than 2000 compounds are currently available and in many cases unknown values can be estimated using simple combining rules [23,30]. The solvent properties r , s , a , b , and l are unambiguously defined: the r constant refers to the ability of a solvent to interact with solute n - or π -electrons; the s constant to the ability of the solvent to take part in dipole–dipole and dipole-induced dipole interactions; the a constant is a

measure of the hydrogen-bond basicity of the solvent; the b constant is a measure of the hydrogen-bond acidity of the solvent; and the l constant incorporates contributions from solvent cavity formation and solute–solvent dispersion interactions, and more specifically in gas–liquid chromatography indicates how well the phase will separate members of an homologous series. For an uncharacterized phase the solvent properties r , s , a , b , and l are determined from the experimentally derived gas–liquid partition coefficients for a minimum of 15 to 30 varied solutes, with known explanatory variables, using the statistical analysis technique of multiple linear regression analysis.

2. Experimental

Di-*n*-octyl phthalate and Chromosorb W-AW (177–250 μm) were obtained from Anspec (Ann Arbor, MI, USA). Tetrachlorophthalic anhydride, *n*-octanol, and 4-toluenesulfonic acid were obtained from Aldrich (Milwaukee, WI, USA). All solvents were OmniSolv grade from EM Science (Gibbstown, NJ, USA). The solutes in Table 1 were obtained from several sources and were of the highest purity generally available.

2.1. Synthesis of di-*n*-octyl tetrachlorophthalate [15,31]

A mixture of tetrachlorophthalic anhydride (17.15 g, 0.06 moles), *n*-octanol (23.40 g, 0.18 moles), 4-toluenesulfonic acid (1.0 g) and benzene (4 ml) were stirred and heated in a 500 ml round-bottomed flask fitted with a thermometer and Dean–Stark trap with a water-cooled condenser. The mixture was heated for 18 h over which time the temperature was raised to 170°C in stages. After 6 h and 12 h a further amount of 4-toluenesulfonic acid (0.5 g) and benzene (2 ml) were added. The mixture turned from colorless to light yellow at 120°C and, over a 15-h period at 150°C, about 7 ml of water was collected in the Dean–Stark trap. For the remaining 3 h of the reaction the temperature was allowed to reach 170°C to distill off volatile material. The reaction mixture was allowed to cool to room temperature and was then extracted with 100 ml of 6% (w/v) sodium

Table 1
Solute and their descriptors used in Eq. 2

Solute	R_2	π_2^H	α_2^H	β_2^H	Log L^{16}
<i>n</i> -Heptane	0.000	0.00	0.00	0.00	3.173
<i>n</i> -Octane	0.000	0.00	0.00	0.00	3.677
<i>n</i> -Nonane	0.000	0.00	0.00	0.00	4.182
<i>n</i> -Decane	0.000	0.00	0.00	0.00	4.686
<i>n</i> -Undecane	0.000	0.00	0.00	0.00	5.191
<i>n</i> -Dodecane	0.000	0.00	0.00	0.00	5.696
<i>n</i> -Tridecane	0.000	0.00	0.00	0.00	6.200
Pentan-2-one	0.143	0.68	0.00	0.51	2.755
Hexan-2-one	0.136	0.68	0.00	0.51	3.262
Heptan-2-one	0.123	0.68	0.00	0.51	3.760
Octan-2-one	0.108	0.68	0.00	0.51	4.257
Nonan-2-one	0.119	0.68	0.00	0.51	4.735
Methyl hexanoate	0.080	0.60	0.00	0.45	3.874
Methyl heptanoate	0.079	0.60	0.00	0.45	4.356
Methyl octanoate	0.065	0.60	0.00	0.45	4.838
Methyl nonanoate	0.056	0.60	0.00	0.45	5.321
Methyl decanoate	0.053	0.60	0.00	0.45	5.803
Butan-1-ol	0.224	0.42	0.37	0.48	2.601
Pentan-1-ol	0.219	0.42	0.37	0.48	3.106
Hexan-1-ol	0.210	0.42	0.37	0.48	3.610
Heptan-1-ol	0.211	0.42	0.37	0.48	4.115
Octan-1-ol	0.199	0.42	0.37	0.48	4.619
Nonan-1-ol	0.193	0.42	0.37	0.48	5.124
2-Methylpentan-2-ol	0.169	0.30	0.31	0.60	3.081
Oct-2-yne	0.225	0.30	0.00	0.10	3.850
Dodec-1-yne	0.133	0.23	0.13	0.10	5.657
1-Nitropropane	0.242	0.95	0.00	0.31	2.894
1-Nitropentane	0.212	0.95	0.00	0.29	3.938
Nitrocyclohexane	0.441	0.97	0.00	0.31	4.826
1,1,2,2-Tetrachloroethane	0.595	0.76	0.16	0.12	3.803
Nonanal	0.150	0.65	0.00	0.45	4.856
1,4-Dioxane	0.329	0.75	0.00	0.64	2.892
1,4-Benzodioxan	0.874	1.01	0.00	0.80	4.985
Benzene	0.610	0.52	0.00	0.14	2.786
Toluene	0.601	0.52	0.00	0.14	3.325
Ethylbenzene	0.613	0.51	0.00	0.15	3.778
<i>n</i> -Butylbenzene	0.600	0.51	0.00	0.18	4.289
Benzonitrile	0.742	1.11	0.00	0.33	4.039
Nitrobenzene	0.871	1.11	0.00	0.28	4.557
Chlorobenzene	0.718	0.65	0.00	0.07	3.657
Bromobenzene	0.882	0.73	0.00	0.09	4.041
Iodobenzene	1.188	0.82	0.00	0.12	4.502
1,2-Dichlorobenzene	0.872	0.78	0.00	0.04	4.518
Benzaldehyde	0.820	1.00	0.00	0.39	4.008
Acetophenone	0.818	1.01	0.00	0.48	4.501
Phenol	0.805	0.89	0.60	0.31	3.766
4-Cresol	0.820	0.87	0.57	0.32	4.312
Methyl phenyl ether	0.708	0.74	0.00	0.29	3.890

bicarbonate solution. Because unreacted acid and monoester tended to solvate the product in the aqueous phase, the aqueous solution was back extracted with 10 ml of benzene. The organic layers were combined, diluted with a further 30 ml of benzene, re-extracted with sodium bicarbonate solution, and solvent and volatile impurities were removed by distillation for 3 h at 40 mm Hg and 45°C. The di-*n*-octyl tetrachlorophthalate ester was obtained as a light yellow oil at a yield of 43%. Purity was confirmed by thin-layer chromatography using the solvent system hexane–chloroform (95:5, v/v) on silica gel (R_F value for diester=0.20). The structure was confirmed by IR and NMR spectroscopy. IR (cm^{-1}), neat liquid sandwiched between sodium chloride plates, 2915, 2852, 1738, 1527, 1456, 1344, 1246, 1168, 1105, 949, 750, and 661. NMR ^1H (ppm), solvent chloroform-*d*, 4.30 (triplet, 4H), 1.70 (multiplet, 20H), 1.28 (multiplet, 4H) and 0.95 (triplet, 6H). NMR ^{13}C 163.77, 135.66, 132.35, 130.40, 77.47, 77.04, 76.62, 70.92, 66.99, 31.74, 29.25, 29.45, 29.77, 29.32, 29.13, 26.19, 25.32, 25.92, 22.59 and 14.01.

2.2. Density determination

The density of di-*n*-octylphthalate and di-*n*-octyl tetrachlorophthalate were determined over the temperature range 60–120°C, using a modified Lipkin bicapillary pycnometer as described previously [32]. The data were fitted to Eq. 3.

$$\rho_t = A - B(t) \quad (3)$$

where ρ_t is the liquid density at temperature t (°C) and A and B are regression coefficients. For di-*n*-octyl phthalate $A = 0.9796$ and $B = 6.2 \times 10^{-5}$ ($r^2 = 0.999$, S.E.=0.00003). For di-*n*-octyl tetrachlorophthalate $A = 1.2600$ and $B = 9.145 \times 10^{-4}$ ($r^2 = 1.000$, S.E.=0.0008).

2.3. Determination of the gas–liquid partition coefficients

The protocol used to determine the gas–liquid partition coefficients is outlined in reference [33] along with a statistical evaluation of the expected precision. Briefly, all measurements were made on

packed columns with a stationary phase loading of 8–20% (w/w) on Chromosorb W-AW (177–250 μm). A minimum of four phase loadings for each phase covering the above range were used to determine the gas–liquid partition coefficients by linear extrapolation to an infinite phase volume based on Eq. 4.

$$V_N^*/V_L = K_L + (\text{adsorption})(1/V_L) \quad (4)$$

where “adsorption” is a composite term representing the sum of all possible interfacial adsorption retention mechanisms. The experimental conditions are selected so that a linear extrapolation can be used as explained elsewhere [33]. The typical uncertainty in K_L is 2–5% relative standard deviation when the uncertainty in the phase loading is $\pm 0.15\%$ (determined by exhaustive Soxhlet extraction), carrier gas flow-rate ± 0.20 ml/min, column pressure drop ± 1 mmHg, column temperature $\pm 0.2^\circ\text{C}$ and retention time ± 0.02 min.

The experimental specific retention volume, $V_g^\circ(\text{ex})$, which includes contributions from all retention mechanisms, was determined using Eq. 5

$$V_g^\circ(\text{ex}) = 273.2V_N/w_L T_c \quad (5)$$

where V_N is the net retention volume, w_L is the weight of liquid phase in the column and T_c is the column temperature. The specific retention volume for gas–liquid partitioning only, $V_g^\circ(\text{part})$, was determined using Eq. 6.

$$V_g^\circ(\text{part}) = 273.2K_L/T_c \rho_c \quad (6)$$

where ρ_c is the liquid phase density at the column temperature. The contribution of interfacial adsorption to the retention mechanism was evaluated by defining the difference in the contribution of interfacial adsorption to the specific retention volume, $V_g^\circ(\text{ads})$, as

$$V_g^\circ(\text{ads}) = V_g^\circ(\text{ex}) - V_g^\circ(\text{part}) \quad (7)$$

which, for convenience, can be expressed as a percentage i.e., as $100 V_g^\circ(\text{ads})/V_g^\circ(\text{ex})$.

2.4. Instrumentation

Gas chromatographic measurements were made using a Varian 3700 gas chromatograph (Walnut Creek, CA, USA) fitted with a flame ionization detector. A mercury manometer was used to measure the column inlet pressure and a US National Institute of Standards and Technology (NIST)-certified thermometer ($\pm 0.2^\circ\text{C}$) was used to measure ambient and column temperatures.

Multiple linear regression analysis was performed on an Epson Apex 200 computer (Epson America, Torrance, CA, USA) using the program SPSS/PC+ V3.1 (SPSS, Chicago, IL, USA). The explanatory variables used in the data analysis are summarized in Table 1 and were taken from the compilations of Abraham and co-workers [23,30,34,35].

3. Results and discussion

The retention mechanism in gas–liquid chromatography involves contributions from gas–liquid partitioning (absorption) as well as contributions from interfacial adsorption at the gas–liquid and liquid–solid interface. The relative contributions of the absorption and adsorption mechanisms are intrinsic properties of the individual solvent (stationary liquid phase) and solute, as well as the experimental parameters such as support properties (surface area, structure, activity, etc.), phase loading, and temperature. When determining solvation properties by gas–liquid chromatography it is important that contributions from interfacial adsorption are excluded from consideration to avoid an over-assessment of the magnitude of the solvent property being determined. General guidelines for predicting the importance of interfacial adsorption as a retention mechanism under different experimental conditions have been provided [19,36], but in general, it is necessary to make a determination of its contribution through Eq. 1 before any certainty can be attached to the retention data generated when the object is to determine solution properties.

Fig. 1 presents some typical data for a varied group of solutes on di-*n*-octyl phthalate at 61.2°C . These solutes are retained by a mixed retention

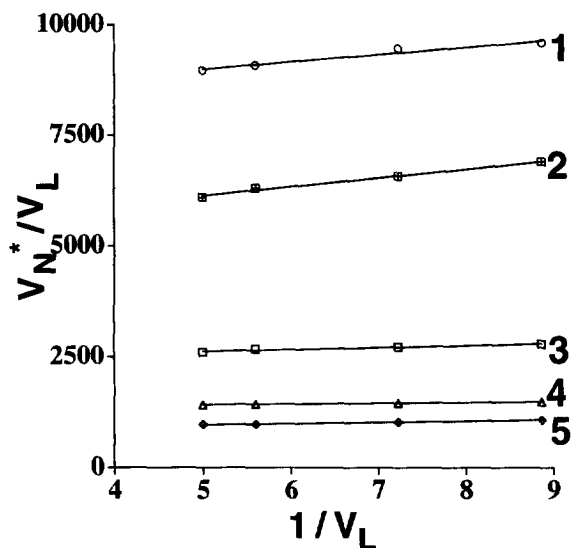


Fig. 1. Plot of V_N^*/V_L against $1/V_L$ for different solutes on di-*n*-octyl phthalate coated onto Chromosorb W-AW at 61.2°C. Identification: 1=benzotrile; 2=benzaldehyde; 3=*n*-decane; 4=ethylbenzene and 5=hexan-2-one.

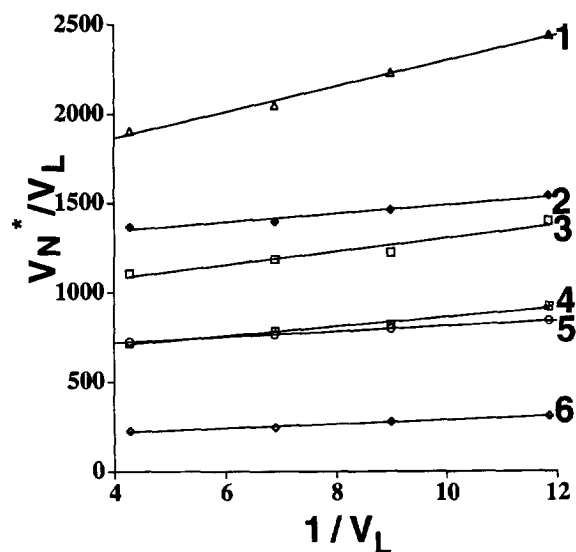


Fig. 2. Plot of V_N^*/V_L against $1/V_L$ for different solutes on di-*n*-octyl tetrachlorophthalate coated onto Chromosorb W-AW at 121.2°C. Identification: 1=nonan-1-ol; 2=acetophenone; 3=*n*-undecane; 4=benzotrile; 5=*n*-butylbenzene and 6=heptan-2-one.

mechanism as indicated by the slope of the line (if retention resulted simply from gas-liquid partitioning the lines would be parallel to the abscissa). Similarly, we present some typical data for a varied group of solutes on di-*n*-octyl tetrachlorophthalate at 121.2°C, Fig. 2. Again these solutes are retained by a mixed retention mechanism. To judge the contribution of interfacial adsorption to retention under different experimental conditions some representative examples are summarized in Table 2. In nearly all cases interfacial adsorption makes an important contribution to retention and, in some cases, it is more important than gas-liquid partitioning. The contribution from interfacial adsorption as a function of phase loading indicates that this contribution declines as the phase loading increases. This is not unexpected since the volume of liquid phase increases with the phase loading, driving a relative increase in the importance from gas-liquid partitioning while the accessible support surface area and gas-liquid interfacial area are not expected to increase to the same extent as the phase loading is increased. There are several instances in Table 2 where the relative contribution from interfacial adsorption increases at higher temperatures, the oppo-

Table 2

Contribution of interfacial adsorption (%) to the retention of some typical solutes on di-*n*-octyl phthalate and tetrachlorophthalate at two temperatures

Compound	Stationary phase			
	Di- <i>n</i> -octyl phthalate		Di- <i>n</i> -octyl tetrachlorophthalate	
	Phase loading (%)			
	8.55	14.40	8.42	15.80
<i>Temperature 61.2°C</i>				
Decane	14.1	7.9	42.3	21.9
Ethylbenzene	10.1	5.8	32.6	15.5
Heptan-2-one	20.4	12.5	63.8	39.7
Methyl heptanoate	14.4	8.5	65.4	42.6
Benzotrile	15.1	9.1	35.3	17.9
Benzaldehyde	25.8	15.9	62.1	38.5
Hexan-1-ol	28.8	18.9	41.2	21.2
<i>Temperature 121.2°C</i>				
Decane	24.9	15.5	46.4	24.9
Ethylbenzene	10.1	6.0	23.6	9.8
Heptan-2-one	28.0	18.1	44.9	23.7
Methyl heptanoate	24.0	15.2	38.5	19.1
Benzotrile	5.3	2.9	35.3	16.5
Benzaldehyde	12.4	7.4	18.4	8.0
Hexan-1-ol	14.0	8.6	42.6	20.0

site behavior to what might be termed the expected trend [19]. In general, this is a case of the relative reduction in the contribution of interfacial adsorption declining with temperature less than the contribution from gas–liquid partitioning resulting in an amplification of the relative importance of interfacial adsorption at the higher of the two temperatures reported in Table 2. Interfacial adsorption played only a small role in the retention of a wide range of solutes on di-*n*-decyl phthalate when a silanized support was used for the measurements [37]. The above factors suggest, but do not prove unequivocally, that adsorption at the support–liquid rather than the gas–liquid interface is the dominant cause of the interfacial adsorption and is a clear indication of the importance of assessing all contributions to retention by gas chromatography when making solution measurements. The relative contribution of interfacial adsorption with different support types, phase loadings and temperatures is one potential source of variation among the reported retention data and its interpretation for the di-*n*-alkyl tetrachlorophthalate stationary phases.

The gas–liquid partition coefficients for the sol-

utes identified in Table 1, corrected for the contribution to retention from interfacial adsorption, were fitted to the solvation parameter model, Eq. 2, giving the characteristic phase constants and statistics for the fit summarized in Table 3. The standard error in the estimate of $\log K_L$ from 0.021 to 0.034 log units and the general statistics indicate that the model provides a good representation of the experimental data. For interpretive purposes we will look at the general solvent properties of the two stationary phases at 121.2°C first and then comment on the influence of temperature on their solution behavior.

In agreement with chemical intuition, neither of the stationary phases is a hydrogen-bond acid, the *b*-constant is statistically insignificant, since there are no suitable hydrogen-bond donor atoms in their structure. Both phases are intermediate hydrogen-bond bases with a weak to intermediate capacity for dipole-type interactions [16]. Di-*n*-octyl tetrachlorophthalate has a significantly weaker capacity for dipole-type interactions than does the di-*n*-octyl phthalate stationary phase. The di-*n*-octyl phthalate ester has no significant capacity as an acceptor of *n*- or π -electrons, the *r*-constant is statistically zero,

Table 3
Summary of the results from multiple linear regression analysis

Temperature (°C)	Phase constants					Statistics ^a			
	<i>c</i>	<i>r</i>	<i>s</i>	<i>a</i>	<i>l</i>	<i>R</i>	S.D.	<i>F</i>	<i>n</i>
<i>Di-n-octyl phthalate</i>									
61.2	-0.253 (0.028)		0.928 (0.014)	1.289 (0.033)	0.775 (0.007)	0.999	0.023	5382	33
81.2	-0.200 (0.028)		0.849 (0.014)	1.122 (0.030)	0.673 (0.006)	0.999	0.029	4956	38
101.2	-0.268 (0.019)		0.808 (0.010)	1.054 (0.021)	0.628 (0.004)	0.999	0.021	10529	46
121.2	-0.275 (0.025)		0.797 (0.013)	1.004 (0.025)	0.571 (0.005)	0.999	0.027	4752	46
<i>Di-n-octyl tetrachlorophthalate</i>									
61.2	-0.106 (0.035)	0.215 (0.021)	0.574 (0.022)	1.452 (0.036)	0.689 (0.008)	0.998	0.031	2187	34
81.2	-0.213 (0.032)	0.187 (0.187)	0.560 (0.022)	1.271 (0.035)	0.682 (0.007)	0.998	0.033	2692	41
101.2	-0.673 (0.023)	0.188 (0.015)	0.582 (0.016)	0.971 (0.026)	0.678 (0.005)	0.999	0.028	5599	46
121.2	-0.475 (0.032)	0.203 (0.020)	0.590 (0.022)	0.740 (0.031)	0.607 (0.006)	0.998	0.034	2444	46

^a*R*=multiple correlation coefficient; S.D.=standard deviation in the estimate; *F*=Fischer *F* statistic; and *n*=number of solutes. The numbers in brackets represent the standard deviation in the characteristic phase constant.

while the tetrachlorophthalate phase is, at best, a weak acceptor. At 121.2°C it has a similar capacity as an n - or π -electron acceptor as the common stationary phases OV-22 and OV-25 [poly-(methylphenyldiphenylsiloxane)s], OV-275 [poly-(dicyanoallylsiloxane)], PPE-5 [1,3-bis(3-phenoxyphenoxy)benzene], and DEGS [poly(diethylene glycol succinate)] [16]. In this sense, its capacity to function as an electron acceptor in charge-transfer complexation interactions can not be considered exceptional, and although these interactions may contribute to the general suite of interactions that occur in the formation of complexes, they can not be perceived as being the dominant intermolecular forces involved. From the values for the l -constant and the c -constant both phthalate esters have a low cohesive energy and cavity formation is relatively easy. In summary, the di- n -octyl tetrachlorophthalate has a greater capacity for n - and π -electron donor interactions than does the di- n -octyl phthalate but the di- n -octyl phthalate is a stronger hydrogen-bond base, has a greater capacity for dipole/polarizability interactions, and is a less cohesive solvent at 121.2°C.

The influence of temperature on the characteristic phase constants of the solvation parameter model within the temperature range 60 to 120°C is best explored graphically. For di- n -octyl phthalate the s -, a -, and l -constant decrease with increasing temperature while the c -constant becomes increasingly negative, Fig. 3. For di- n -octyl tetrachlorophthalate similar trends are observed except that in this case the change in the c - and a -constants is much more marked while the r - and s -constants are virtually unchanged, within experimental error, Fig. 4. These facts have some significant bearing on the characterization of the solution properties of the two phthalates. Whereas di- n -octyl tetrachlorophthalate is a stronger hydrogen-bond base than di- n -octyl phthalate at 121.2°C this is not true for temperatures below 100°C; the difference in capacity of the two phthalates for dipole-type interactions is significantly greater at 60°C than 120°C. When considering the relative capacity of solvents for intermolecular interactions, it is obvious that a snap-shot at a single temperature can be quite misleading if it is intended to use that information as a general guide for solution behavior at significantly different temperatures.

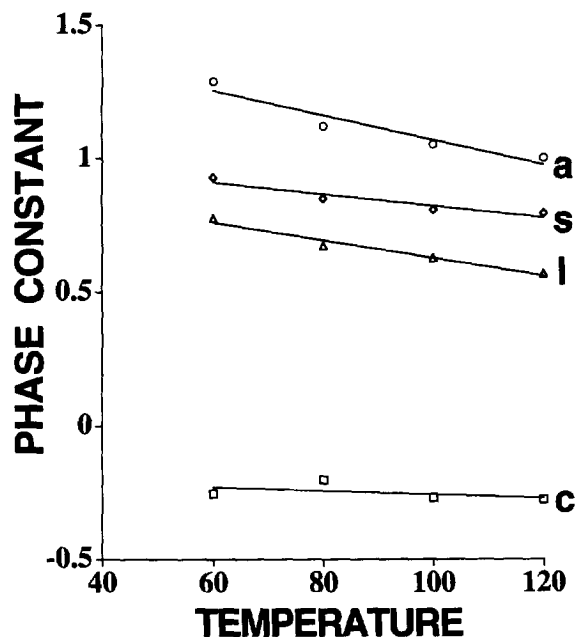


Fig. 3. Plot of the characteristic phase constants vs. temperature for di- n -octyl phthalate.

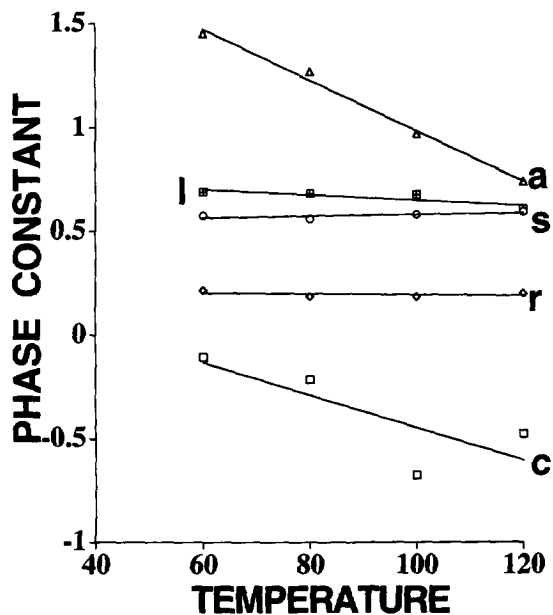


Fig. 4. Plot of the characteristic phase constants vs. temperature for di- n -octyl tetrachlorophthalate.

Table 4
Contribution of different intermolecular interactions to retention ($\log K_L$) for some representative compounds on the phthalate ester stationary phases

Solute	Temperature (°C)	Stationary phase						
		Di- <i>n</i> -octyl phthalate			Di- <i>n</i> -octyl tetrachlorophthalate			
		$s\pi_2^H$	$a\alpha_2^H$	$\sum(c + l \log L^{16})$	rR_2	$s\pi_2^H$	$a\alpha_2^H$	$\sum(c + l \log L^{16})$
Ethylbenzene	61.2	0.48		2.684	0.13	0.30		2.505
	122.2	0.41		1.889	0.12	0.31		1.825
Chlorobenzene	61.2	0.60		2.581	0.15	0.37		2.414
	121.2	0.52		1.813	0.15	0.38		1.745
Iodobenzene	61.2	0.76		3.236	0.26	0.47		2.996
	121.2	0.65		2.296	0.24	0.48		2.258
Benzyl alcohol	61.2	0.81	0.43	4.552	0.17	0.50	0.48	4.166
	121.2	0.69	0.33	3.265	0.16	0.51	0.24	3.288
Benzonitrile	61.2	1.03		2.877	0.16	0.64		2.783
	121.2	0.88		2.031	0.15	0.65		1.977
Heptan-2-one	61.2	0.63		2.611	0.03	0.39		2.485
	121.2	0.54		1.872	0.03	0.40		1.807
Hexan-1-ol	61.2	0.39	0.48	2.545	0.05	0.24	0.54	2.381
	121.2	0.33	0.37	1.786	0.04	0.25	0.27	1.716
1-Nitropropane	61.2	0.88		2.799	0.05	0.55		2.607
	121.2	0.76		1.974	0.04	0.56		1.915

The breakdown of the contribution of individual intermolecular forces to retention for some representative compounds provides a clear indication of the dominant forces responsible for selective solvation in the phthalate ester phases, Table 4. The opposing contributions from cavity formation in the solvent and dispersion interactions between the solute and solvent are represented by the sum of $(c + l \log L^{16})$ shown in Table 4. This can not be an exact assessment since the c -constant contains contributions related to the lack of fit for the model but, as demonstrated in previous studies, the sum term is a better representation of the cavity and dispersion contributions than the $l \log L^{16}$ term alone [25,26,35,38]. For now, we have no exact method to dissect the product $\sum(c + l \log L^{16})$ into precisely defined contributions of cavity formation and dispersion interactions [27]. As illustrated by the data in Table 4 (and also all the solute data collected in these studies), the dominant interactions between solutes and the phthalate ester solvents are dispersion interactions, which easily exceed the opposing requirements for cavity formation in the solvent, at least for the temperature range studied (60 to 120°C). The

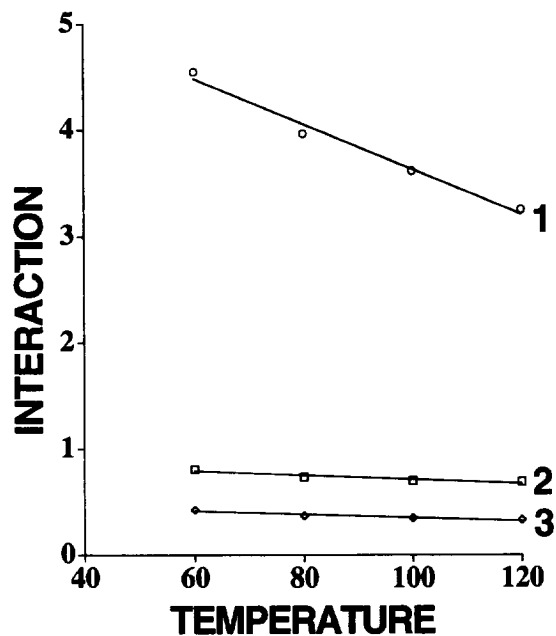


Fig. 5. Contribution from individual intermolecular interactions to the gas-liquid partition coefficient of benzyl alcohol, on di-*n*-octyl phthalate as a function of temperature. Identification: 1= contribution from cavity formation and dispersion interactions; 2=contribution from dipole-type interactions and 3=solute hydrogen-bond acid/solvent hydrogen-bond base interactions.

influence of polar interactions is significantly less marked. Consider the case of benzyl alcohol, by way of example, on di-*n*-octyl phthalate (Fig. 5) and di-*n*-octyl tetrachlorophthalate (Fig. 6). Benzyl alcohol is a moderate *n*- and π -electron donor ($R_2 = 0.803$) and has an intermediate capacity for dipole/polarizability ($\pi_2^H = 0.87$) and hydrogen-bond acid ($\alpha_2^H = 0.33$) interactions (its capacity to function as a hydrogen-bond base is immaterial since neither phase is a hydrogen-bond acid, b -constant=0). The contribution of dipole/polarizability interactions ($s\pi_2^H$) and solvent hydrogen-bond base/solute hydrogen-bond acid interactions ($a\alpha_2^H$) to $\log K_L$ is small when normalized against the sum term representing the contribution of cavity formation and dispersion interactions. The contribution from *n*- and π -electron complexation (rR_2) on the tetrachlorophthalate phase is small and of a magnitude similar to dipole/polarizability and solvent hydrogen-bond base/solute hydrogen-bond acid interactions, over the tempera-

ture range studied, but is by no means as important as the contribution from dispersion interactions. Iodobenzene was the strongest *n*- and π -electron donor in the data set ($R_2 = 1.188$) but its interactions with the tetrachlorophthalate phase (Fig. 7) are again dominated by the contribution of cavity formation and dispersion interactions. In all cases, at least for the temperature range studied, complexes formed between the phthalate esters and aromatic solutes are likely to be predominantly of the Van der Waals type involving dispersion interactions, perhaps enhanced by *n*- or π -electron charge transfer or dipole-type interactions. In general the range of chromatographic selectivity obtainable, through exploitation of the phthalate and tetrachlorophthalate nucleus, does not warrant their selection as building blocks for new polymer-supported phases with the expectation of providing opportunities to extend the selectivity range of existing gas chromatographic stationary phases.

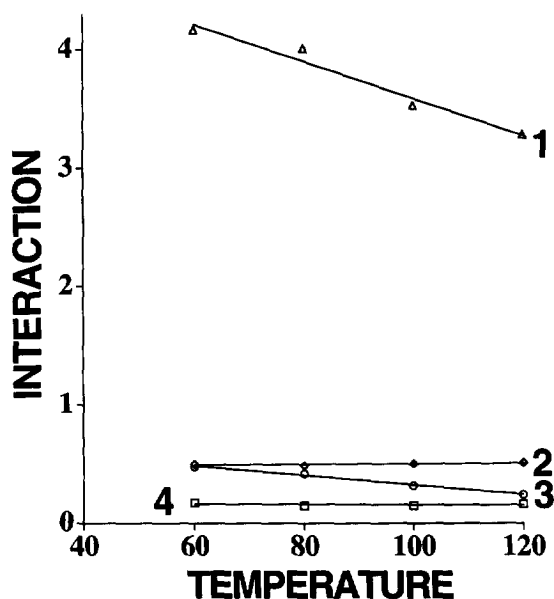


Fig. 6. Contribution from individual intermolecular interactions to the gas-liquid partition coefficient of benzyl alcohol on di-*n*-octyl tetrachlorophthalate as a function of temperature. Identification: 1=contribution from cavity formation and dispersion interactions; 2=contribution from dipole-type interactions; 3=contribution from solute hydrogen-bond acid/solvent hydrogen-bond base interactions and 4=contribution from solute *n*- and π -electron donor/solvent acceptor interactions.

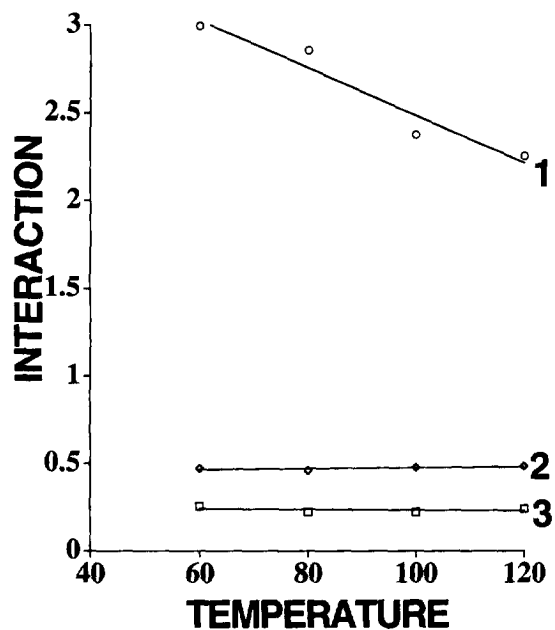


Fig. 7. Contribution from individual intermolecular interactions to the gas-liquid partition coefficient of iodobenzene on di-*n*-octyl tetrachlorophthalate as a function of temperature. Identification: 1=contribution from cavity formation and dispersion interactions; 2=contribution from dipole-type interactions and 3=contribution from solute *n*- and π -electron donor/solvent acceptor interactions.

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