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## EXPERIMENTAL PROTOCOL FOR THE ASSESSMENT OF SOLVENT STRENGTH AND SELECTIVITY OF LIQUID PHASES USED IN GAS CHROMATOGRAPHY

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### SUMMARY

A thermodynamic approach to the practical characterization of solvent strength and selectivity of a wide range of molecular and ionic stationary phases for gas chromatography is discussed. The experimental protocol is outlined in detail and the principal sources of error with their magnitude identified. The solvent strength parameter (the partial molar Gibbs free energy of solution for a methylene group per unit solvent volume) is proposed as a universal parameter for measuring solvent strength although it is indicated that in the general ranking of liquid phases anomalous positioning of ionic phases and perfluorocarbon phases may occur. The partial molal Gibbs free energy of solution for selected test solutes is proposed as a scale of solvent selectivity. Nitrobenzene and *n*-octanol are demonstrated to be acceptable test solutes to characterize solvent orientation and proton acceptor capacity, respectively. Benzodioxan is shown to be an unacceptable test solute for assessing solvent proton donor capacity and dibutylformamide is tentatively identified as a promising replacement. Tabulation of the above constants provides new insight into the solvent properties of the most common liquid phases used in gas chromatography. In particular, it is demonstrated that the liquid organic salts provide enhanced orientation and proton acceptor capacity compared to non-ionic liquids and represent an important class of new solvents for extending the selectivity range of solvents used in gas chromatography. A need for new phases with strong proton donor capacity is also identified.

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### INTRODUCTION

The ease of obtaining a particular separation in gas-liquid chromatography is primarily a function of the difference in volatility of the analytes and the difference in the sum of the total intermolecular interactions between the analyte and the stationary liquid phase<sup>1</sup>. Solute-mobile phase interactions, by comparison, are relatively small for typical gases and normal column operating conditions in gas chromatography. For samples comprised of analytes of significantly different volatility a high efficiency, non-selective, liquid phase column should be all that is required to achieve the desired

separation of the mixture. In all other cases a selective liquid phase will be required to separate the analytes based on the difference in residence time for the individual analytes in the stationary liquid phase. This approach will depend entirely on having available a suitable stationary phase with properties complementary to those of the analytes and the existence of some difference, albeit small, in the capacity of the analytes to enter into specific intermolecular interactions. For these types of separation problems we need a number of liquid phases having different solvent characteristics. The exact number of needed (useful) phases is unspecified but is certainly less than the voluminous number of known phases since many of these possess properties that if not duplicates of each other are very similar in their separation characteristics. There is a problem of sensible stationary phase selection exacerbated by the absence of a reliable criteria for identifying a manageable number of preferred stationary phases encompassing the widest range of solvent characteristics.

The characteristics of a stationary phase that dictate its selection as a preferred phase are its useful temperature operating range, ability to provide columns of acceptable efficiency and its characteristics as a solvent determined by its solvent strength and selectivity. The first two parameters can be measured unambiguously and limiting boundary conditions established<sup>2</sup>. The solvent strength and solvent selectivity criteria cannot be defined unambiguously since there is no complete physical model that can adequately describe the concert of intermolecular interactions that takes place between complex molecules under conditions germane to the gas chromatographic experiment. Practical solutions to this problem have been sought by chromatographers who have come to rely on empirical approaches to categorise these forces<sup>2,3</sup>. The principal forces that exist between molecules are dispersion, induction, orientation and donor-acceptor complexation (*e.g.*, hydrogen bonding). The strength of a solvent is a measure of its capacity to enter into all possible interactions. It is synonymous with the term polarity and although a reasonable understanding of what is implied by this term exists, it is not an easy task to define in a totally unambiguous manner. Solvent selectivity is a measure of the relative importance of dispersion, induction, orientation and donor-acceptor complexation to the solvent strength and is the more useful criterion for solvent selection.

Various empirical scales have been proposed to characterize common liquid phases in terms of their solvent strength (polarity)<sup>3-6</sup>. The principal feature of these scales was the desire to define a single parameter suitable for ranking phases by their capacity for all types of selective interactions. Those scales based on the relative retention of two solutes, one of which was usually a hydrocarbon, or retention index values of polar solutes such as alcohols or dipolar and polarizable solutes are of dubious value<sup>4-11</sup>. In the first place, their interactions with the liquid phase are weighted in favor of the specific interaction dominating the property of the test solute. Secondly, the magnitude of the retention index value is strongly dependent on the solubility of the retention index standards in the stationary phase as well as the specific interaction of the test solute with the stationary phase. This is the reason why McReynolds'  $P_m$  value [sum of first five of McReynolds' selectivity indices (benzene, *n*-butanol, nitropropane, 2-pentanone and pyridine)], Snyder's  $P'$  value (sum of the logarithms of the corrected solute distribution coefficients for ethanol, dioxane and nitromethane) and the polarity index show a strong correlation with the chroma-

tographic properties of the hydrocarbons themselves, such as with the partial molar Gibbs free energy of solution for a methylene group<sup>12-17</sup>. Alternative approaches are based on chemometric methods, such as principal component analysis, applied to the retention index data of McReynolds<sup>8</sup>. The limitations of this approach are deficiencies in the retention index data discussed above and the rather vague physical description of the interpretation of the results<sup>18</sup>. Probably the most reasonable and acceptable measure of solvent strength is given by the reluctance of a stationary phase to dissolve a hydrocarbon expressed as the ratio of retention time differences for adjacent *n*-alkanes<sup>13,18,19</sup>, the partial molar Gibbs free energy of solution for a methylene group<sup>12,17,19-27</sup> and the solvent strength parameter (the partial molar Gibbs free energy of solution for a methylene group per unit solvent volume)<sup>27</sup>. These scales should be closely related but literature values may vary due to neglect of the contribution made by interfacial adsorption to retention, particularly for *n*-alkane standards on polar phases.

Solvent selectivity scales for gas-liquid chromatography abound, the most common ones being the system of phase constants proposed by Rohrschneider and later modified by McReynolds<sup>3,28-32</sup>, Snyder's solvent selectivity triangle<sup>11,17,33,34</sup>, dispersion selectivity indices<sup>35-37</sup>, Hawkes' polarity indices<sup>38</sup>, solubility parameters<sup>39,40</sup>, solvatochromic parameters<sup>41,42</sup> and several thermodynamic approaches<sup>4,17,21,23,27,43-47</sup>. These methods and others are reviewed elsewhere<sup>3,4,23</sup>. The McReynolds system of phase constants has become the most widely used systematic approach to solvent selectivity characterization and virtually all popular stationary phases have been characterized by this method. In recent years it has become obvious that the McReynolds approach is flawed for a combination of theoretical and practical reasons which can be briefly summarized as follows: poor retention of test solutes on some phases prevents the accurate determination of retention index values; the calculation method ignores the importance of interfacial adsorption as a retention mechanism (interfacial adsorption is often the dominant retention mechanism for *n*-alkanes on polar phases); individual phase constants are composite values defined by the retention characteristics of both the retention index standards and test solutes (the retention characteristics of the *n*-alkanes dominate in many cases) and the original data of McReynolds contain experimental uncertainties which affect their reliability<sup>3,14-17,26-28,46-49</sup>. The above comments are also relevant to the use of other methods such as Snyder's selectivity triangle and dispersion indices which are based on the use of the retention index system. The retention index system is a reliable method for characterizing retention on a specific phase, when interfacial adsorption is absent, but is not appropriate for determining solvent selectivity by comparing index measurements on different phases. To avoid this problem absolute retention properties of suitably selected test solutes have to be used. Thermodynamic approaches, based on the experimentally determined gas-liquid partition coefficient, seem to be the most appropriate alternative to the previously used phase constants. Risby and co-workers<sup>43-45</sup> compared a number of liquid phases using the partial molar or molal Gibbs free energy or enthalpy of solution for different functional groups based on earlier published experimental data of McReynolds. Golovnya and Misharina<sup>23</sup> derived a general relationship between the partial molar Gibbs free energy of solution for McReynolds test solutes and their retention index values. This enabled free energies to be calculated from the retention index values of McReynolds

(approximate values as corrections for differences in solvent densities were not made). However, both of the above approaches are compromised by the unreliability of the experimental data of McReynolds as discussed previously<sup>3,26</sup>. To remove these inconsistencies in the McReynolds data a new set of experimental gas-liquid partition coefficients for a wide range of test solutes have been accurately determined for a large number of common non-ionic and liquid organic salt phases<sup>16,17,26,27,46-52</sup>. The purpose of this paper is to summarize and collect all the relevant published data from the above studies, correct earlier experimental errors in the determination of some constants, add additional unpublished data to the collection, define the rationale followed in establishing the experimental protocol and to indicate the source and magnitude of errors connected with the measurements, and to provide an interpretation of solvent strength and selectivity of a wide range of familiar and novel liquid phases.

## EXPERIMENTAL

Table I lists the stationary phases and common abbreviations used for their identification in the text. The liquid organic salts were prepared by standard methods described elsewhere<sup>16,24,42,48-52</sup>. Di(2-ethylhexyl)phosphoric acid and di(2-ethylhexyl)phosphonate were of technical grade (*ca.* 95%) from Pfaltz and Bauer (Westbury, CT, U.S.A.) and were used as received.

All chromatographic measurements were made using a Varian 3700 gas chromatograph and packed columns prepared from Chromosorb W AW or Gas Chrom Q as described elsewhere<sup>17,24,27</sup>. A mercury manometer was used to measure column inlet pressures and an NBS-certified mercury-in-glass thermometer to measure ambient and column temperatures.

## RESULTS AND DISCUSSION

### *Sources of error in the experimental protocol*

Retention in gas-liquid chromatography can occur by a combination of partition and interfacial adsorption mechanisms involving the bulk liquid, a structured liquid film close to the support surface and the support surface itself<sup>3,17,27,49,53-58</sup>. At high liquid phase loadings the contribution from the structured liquid phase layer can generally be neglected. Likewise, under these conditions it is a generally observed experimental result that the contribution of interfacial adsorption will be dominated by either gas-solid adsorption (non-polar phases on an active support) or by gas-liquid adsorption for polar phases, which generally show good support deactivating characteristics<sup>17,27,46</sup>. The gas-liquid partition coefficient may then be determined by linear regression using eqns. 1 and 2 with experimental data for a minimum of four column packings with different phase loadings.

$$V_N^*/V_L = K_L + B/V_L \quad (1)$$

$$V_N^* = (3/2W)(t_R - t_M)F_0(T_c/T_a)[1 - (P_w/P_a)][(P^2 - 1)/(P^3 - 1)] \quad (2)$$

where  $V_N^*$  is the net retention volume per gram of column packing,  $V_L$  the volume of

TABLE I  
ABBREVIATIONS AND CHEMICAL COMPOSITION OF STATIONARY PHASES

<i>Abbreviation</i>	<i>Chemical composition</i>
Squalane	2,6,10,15,19,23-Hexamethyltetracosane
Apolane-87	24,24-Diethyl-19,29-dioctadecylheptatetracontane
DDP	Didecylphthalate
DEHPA	Di(2-ethylhexyl)phosphoric acid
DEHP	Di(2-ethylhexyl)phosphonate
THPED	N,N,N',N'-Tetrakis(2-hydroxypropyl)ethylenediamine
PPE-5	1,3-Bis(3-phenoxyphenoxy)benzene
Carbowax 20M	Poly(ethylene glycol)
DEGS	Poly(diethylene glycol succinate)
TCEP	1,2,3-Tris(2-cyanoethoxy)propane
SE-30	Poly(dimethylsiloxane)
OV-3	Poly(dimethylmethylphenylsiloxane) containing 10 mol% phenyl groups
OV-7	Poly(dimethylmethylphenylsiloxane) containing 20 mol% phenyl groups
OV-11	Poly(dimethylmethylphenylsiloxane) containing 35 mol% phenyl groups
OV-17	Poly(methylphenylsiloxane)
OV-22	Poly(phenylmethyldiphenylsiloxane) containing 65 mol% phenyl groups
OV-25	Poly(phenylmethyldiphenylsiloxane) containing 75 mol% phenyl groups
OV-105	Poly(cyanopropylmethylmethoxymethylsiloxane)
OV-225	Poly(cyanopropylmethylphenylmethylsiloxane)
OV-275	Poly(dicyanoallylsiloxane)
OV-330	Poly(dimethylsiloxane)/Carbowax copolymer
QF-1	Poly(trifluoropropylmethylsiloxane)
<i>Liquid organic salts</i>	
<i>Cations</i>	
TBMA	Tri- <i>n</i> -butylmethylammonium
QBA	Tetra- <i>n</i> -butylammonium
QBP	Tetra- <i>n</i> -butylphosphonium
TBA	Tri- <i>n</i> -butylammonium
QEA	Tetra- <i>n</i> -ethylammonium
<i>Anions</i>	
OS	Octanesulfonate
CHES	2-(Cyclohexylamino)ethanesulfonate
Cl	Chloride
PTS	4-Toluenesulfonate
CAPS	3-(Cyclohexylamino)-1-propanesulfonate
BuS	Butanesulfonate
MOPS	4-Morpholinepropanesulfonate
HS	Hexanesulfonate
MES	4-Morpholineethanesulfonate
MS	Methanesulfonate
Br	Bromide
NO <sub>3</sub>	Nitrate
PIC	Picrate
BS	Benzenesulfonate
FBS	Pentafluorobenzenesulfonate
MOPSO	2-Hydroxy-4-morpholinepropanesulfonate
BES	2-Bis(2-hydroxyethyl)aminoethanesulfonate
ACES	2-(2-Acetamido)aminoethanesulfonate
I	Iodide
TAPS	3-Tris(hydroxymethyl)methylamino-1-propanesulfonate
TAPSO	3-Tris(hydroxymethyl)methylamino-2-hydroxy-1-propanesulfonate

liquid phase per gram of column packing,  $K_L$  the gas-liquid partition coefficient,  $B$  an integer containing terms characteristic of the magnitude of interfacial adsorption at the support and/or liquid interface ( $B = 0$  for a purely partition system),  $t_R$  the solute retention time,  $t_M$  the column dead time (assumed equal to the retention time of methane at  $T_c$ ),  $F_0$  the carrier gas flow-rate at the column outlet,  $T_c$  the column oven temperature,  $T_a$  the ambient temperature,  $P_w$  the vapor pressure of water at  $T_a$  (assuming a soap-film bubble meter is used to measure flow),  $P_a$  the ambient pressure,  $P$  the column pressure drop  $P_i/P_a$ ,  $P_i$  the column inlet pressure and  $W$  the weight of column packing. The gas-liquid partition coefficient,  $K_L$ , is determined as the intercept on the  $V_N^*/V_L$  axis corresponding to  $1/V_L = 0$  by extrapolation of the experimental data. Errors in  $K_L$  arise primarily from three sources: poor control of the experimental parameters; from the limiting assumptions that apply to eqn. 1 and from the assumption that the gas phase behaves ideally. These errors are accumulative and must be minimized by the choice of experimental protocol<sup>57,59,60</sup>.

Table II summarizes the typical uncertainties associated with the experimental parameters used to determine  $K_L$ . These values are typical of those that can be achieved by simple modification to an analytical gas chromatograph rather than what might be possible for a state-of-the-art high precision instrument used for physicochemical measurements. The set point error in existing pressure gauges and temperature controllers for analytical gas chromatographs is likely very large and thus the need to provide alternative means of determining these parameters with greater accuracy. The existing gauges provide reproducible resetting of conditions but typically contain significant offset errors of about  $\pm 3^\circ\text{C}$  in temperature and  $\pm 2\text{--}3$  p.s.i. in pressure. Temperature gradients across the column axes should be minimized and averaged in computing  $T_c$ .<sup>57,61</sup> With an uncertainty in the temperature measurement of  $\pm 0.2^\circ\text{C}$  temperature gradients should not be a significant source of error for modern high resolution instruments but may be substantial for older packed column instruments. The accumulative errors associated with the uncertainty in the measurement of time, flow, pressure and temperature are generally less important than the errors connected with the determination of  $V_L$ . The accurate determination of phase loadings by either Soxhlet extraction or high-temperature evaporation is the least certain of the experimental parameters that have to be determined and is almost impossible to control to better than 1-2% relative standard deviation (R.S.D.)<sup>24,27,60,62</sup>. This is reflected in the uncertainty in  $K_L$  which is typically 3-5% R.S.D. for  $K_L$  values from 10 to 100 and 2-3% R.S.D. for  $K_L$  values from 100 to 1000.

The density of liquids or melted solids is easily determined with acceptable

TABLE II  
TYPICAL UNCERTAINTIES IN THE EXPERIMENTAL PARAMETERS USED TO DETERMINE  $K_L$

Variable	Uncertainty	Variable	Uncertainty
Time (min)	$\pm 0.02$	Pressure (mmHg)	$\pm 1.0$
Flow-rate (ml/min)	$\pm 0.20$	Density (g/ml)	$\pm 0.0008$
Weight (g)	$\pm 0.0002$	Phase loading (% w/w)	$\pm 0.15$
Temperature ( $^\circ\text{C}$ )	$\pm 0.2$		

TABLE III

REGRESSION COEFFICIENTS FOR THE CALCULATION OF DENSITY USING EQN. 4

Stationary phase	Regression coefficients		Stationary phase	Regression coefficients	
	<i>A</i>	<i>B</i> × 10 <sup>4</sup>		<i>A</i>	<i>B</i> × 10 <sup>4</sup>
Squalane	0.8228	6.014	QBA HS	1.0586	7.250
Apolane-87	0.8650	7.302	QBA MOPS	1.1170	8.043
DDP	0.9827	9.988	QBA MES	1.0726	7.509
DEHPA	1.0053	8.791	QBA MS	1.0421	7.321
DEHP	1.0137	8.602	QBA PIC	1.1608	6.854
THPED	1.0649	7.546	QBA PTS	1.0898	7.397
PPE-5	1.2212	8.553	QBA BS	1.1278	9.466
Carbowax 20M	1.1490	9.494	QBA FBS	1.2368	8.914
DEGS	1.3009	9.969	QBA MOPSO	1.1956	7.968
TCEP	1.1437	9.654	QBA BES	1.1017	6.744
OV-3	1.0444	13.899	QBA ACES	1.1275	8.741
OV-7	1.0713	11.963	QBA TAPS	1.2358	10.150
OV-11	1.1362	11.771	QBA TAPSO	1.1552	8.654
OV-17	1.1312	9.514	TBMA OS	1.0270	8.113
OV-22	1.1741	10.832	TBMA HS	1.0395	7.690
OV-25	1.2305	11.693	TBA PTS	1.1024	8.320
OV-105	1.0209	11.517	QEA PTS	1.1665	7.756
OV-225	1.1098	7.513	QBP CHES	1.0534	7.940
OV-275	1.1723	6.539	QBP Cl	0.9850	6.992
OV-330	1.1605	11.043	QBP PTS	1.1217	7.819
QF-1	1.3025	11.337	QBP MOPS	1.0727	7.871
QBA OS	1.0537	8.509	QBP Br	1.0982	8.079
QBA CAPS	1.0508	7.290	QBP Nitrate	1.0287	6.811
QBA BuS	1.0119	7.396	QBP I	1.4616	10.399
QBA CHES	1.0612	8.459	QBP TAPSO	1.1676	7.527

accuracy using a modified Lipkin bicapillary pycnometer<sup>25</sup>. Density measurements were usually made over the temperature range 65–130°C when permitted by the physical properties of the stationary phase and fitted to

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

The regression coefficients *A* and *B* are summarized in Table III where *t* is the temperature in °C and  $\rho_t$  the density at temperature *t*. The correlation coefficient (*r*) for a linear fit was always greater than 0.990 and generally 1.000. This justifies a linear fit for the data given the average uncertainty in the experimental data, 0.0008 g/ml, and its use to interpolate within the experimental temperature range. Under other conditions an exponential fit might be more appropriate<sup>63</sup>.

Large and variable errors in  $K_L$  can result from a failure to understand the limitations of eqn. 1. This equation is derived assuming that the individual contributions to retention are independent of each other and additive. This will be true when the infinite dilution and zero surface coverage approximations are applicable. That is, for very small sample sizes where the linearity of the various sorption isotherms are likely to be unperturbed and solute-solute interactions are negligible.

These conditions can generally be met with sensitive detectors, such as the flame ionization detector, by the injection of volatile samples as headspace vapors of appropriate volume (1–100  $\mu\text{l}$ , typically 10  $\mu\text{l}$ ). The constancy of the solute retention volume with variation of sample size at low sample sizes and the propagation of symmetrical peaks is a reasonable indication that the above conditions have been fulfilled. Eqn. 1 is not applicable to peaks exhibiting appreciable asymmetry for which alternative calculation methods should be considered<sup>64,65</sup>.

At low phase loadings the liquid phase will coat the support, primarily, as a structured layer with an entropy of solution different from that of the bulk liquid. Eqn. 1 is applicable only if contributions to retention from the structured liquid phase layer can be neglected. At precisely what phase loading this condition is met will depend on the surface area of the support, the liquid phase support wetting characteristics and possibly the column temperature<sup>66–68</sup>. Occasionally modification of eqn. 1 to account for the presence of a structured liquid layer seems unnecessary for phase loadings above 5% (w/w) on typical diatomaceous supports but, more generally phase loadings about 10% (w/w) are required to be certain that this statement is true. In our experience for packings prepared with Chromosorb W AW the useful range of liquid phase loadings for determining  $K_L$  is 7.5 to 17.5% (w/w).

Non-polar phases exhibit little support deactivating characteristics necessitating silanization to obtain symmetrical peak shapes for polar test solutes. It is recommended that the support should be silanized and washed prior to coating and not silanized by the on-column silanization method to avoid contamination of the phase by polymeric impurities in the silanizing reagent<sup>47</sup>. Polar phases do not wet silanized supports well and these supports are not useful for preparing packings with polar phases. On the other hand, polar phases at high phase loadings are good deactivating agents and undesirable support interactions for most solutes are much less of a problem than they are for non-polar phases.

It is reasonable, to a first approximation, to ignore the influence of gas phase non-ideality on retention for the carrier gases and operating conditions commonly employed in gas chromatography. For the most accurate results, however, a correction must be made<sup>69,70</sup>. For operation at a low column pressure drop the corrected gas–liquid partition coefficient for zero column pressure drop,  $K_L(0)$ , is related to the experimental gas–liquid partition coefficient by

$$\ln K_L(0) = \ln K_L - 0.75 [(2B_{12} - V_1^\infty)/RT_c][(P^4 - 1)/(P^3 - 1)] \quad (4)$$

where  $B_{12}$  is the second interaction virial coefficient (solute–carrier gas),  $V_1^\infty$  the solute molar volume at infinite dilution in the solvent, and  $R$  the molar gas constant. Very few experimental virial coefficients are available since they depend on both temperature and the identity of the carrier gas. Approximate values can be calculated by the method of corresponding states which may, in turn, require the input of physical constants unavailable for the conditions of interest, as well as leading to virial constants with an unknown degree of uncertainty. A more practical approach to the problem is to arrange the experimental conditions such that the effect of non-ideal behavior in the gas phase is minimized. From eqn. 4 it can be seen that with a column pressure drop of unity the correction term will be zero. By minimizing the column pressure drop,  $P < 1.5$  atm, the virial correction term will remain small. This is easy to achieve by



using columns of moderate length, 1–2 m, moderate flow-rates, about 20 ml/min, and coarse particle supports, 40–60 or 60–80 mesh. The formation of fines during column preparation procedures should be guarded against for the above reason. Fluidized-bed drying devices are very useful for eliminating fines produced during coating or present in the original support<sup>2,24</sup>. At a low column pressure drop and moderate temperatures the maximum correction to the partition coefficient to account for gas phase non-ideality should be no greater than a few percent and generally should be less than 1%. In the relative sense the correction term is less important since it will be similar in magnitude for all columns and for the purpose of characterizing solvent strength and selectivity its neglect will have little influence on the conclusions reached. It should be noted, however, that while an estimate of the general experimental error can be obtained from the uncertainty determined for  $K_L$  this does not include the additional uncertainty for gas phase non-ideality. Consequently, the most favorable experimental conditions to minimize the column pressure drop should always be selected.

#### General scale of solvent strength

For the purpose of this paper we will define the general scale of solvent strength by the reluctance of a stationary phase to dissolve an *n*-alkane, expressed by the solvent strength parameter. The partition coefficient equivalent to a methylene group is obtained as the slope of a plot of  $\log K_L$  against carbon number for a homologous series of compounds such as *n*-alkanes, 2-alkanones, fatty acid methyl esters, etc. The identity of the homologues is not important provided that the alkane chain length is sufficiently long that the average contribution per methylene group is not significantly influenced by the presence of the functional group<sup>71–73</sup>. This condition is likely to be met for homologues containing four or more methylene groups between the methyl group and the functional group. Treating terminal methyl groups as methylene groups does not introduce a measurable error when the free energy per methylene group is calculated from the slope of  $\log K_L$  against carbon number. The *n*-alkanes are not the preferred standards for the above calculation since on polar phases their retention is frequently dominated by interfacial adsorption (for example, see Fig. 1). Tridecane has

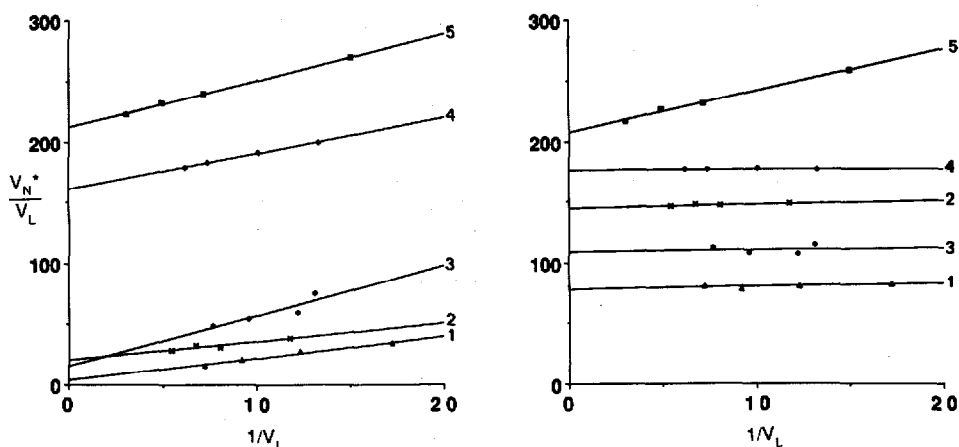


Fig. 1. Plots of  $V_N^*/V_L$  against  $1/V_L$  for *n*-tridecane (left) and 2-octanone (right) at 121°C on a series of polar liquid phases. Identification: 1 = OV-275; 2 = TCEP; 3 = DEGS; 4 = Carbowax 20M; 5 = THPED.

a small partition coefficient on the polar phases that is not well determined by the extrapolation method based on eqn. 1. Plots of  $\log K_L$  against carbon number are frequently scattered for these phases indicating the poor quality of the partition coefficient data. On the other hand, the 2-alkanones are retained almost exclusively by gas-liquid partitioning on all phases and provide  $K_L$  values of larger magnitude and greater precision. In Fig. 1, only THPED shows significant interfacial adsorption in the retention of 2-octanone, and even in this case the partition coefficient is sufficiently large to allow a reasonable determination. It is recommended that the 2-alkanones be adopted as the universal standards to determine the partial molar Gibbs free energy of solution for a methylene group. In those cases where reasonably accurate free energy values are available the difference in values between the *n*-alkane and 2-alkanone standards is generally less than 3% and not significantly different from the experimental error<sup>17,26,27</sup>. An error of 0.01 in the slope of a plot of  $\log K_L$  against carbon number will result in an error of 18 cal/mol in the partial molar Gibbs free energy of solution for a methylene group in Table IV. Thus, differences less than about 10 cal/mol for the non-polar phases and 20 cal/mol for the polar phases are not significant.

TABLE IV

COLLECTION OF SOLVENT STRENGTH PARAMETERS FOR STATIONARY PHASES AT 121°C

Stationary phases	$\Delta G_k^\circ (CH_2)$ (cal/mol)	Solvent strength parameter (cal · cm <sup>3</sup> /g · mol)	Stationary phases	$\Delta G_k^\circ (CH_2)$ (cal/mol)	Solvent strength parameter (cal · cm <sup>3</sup> /g · mol)
Squalane	-521	-716	OV-330	-418	-407
Apolane-87	-518	-667	QBA MOPS	-391	-407
DDP	-511	-592	QBA MES	-398	-406
SE-30	-463	-578	QBA MS	-384	-403
DEHPA	-484	-539	OV-25	-431	-396
DEHP	-490	-539	QBA Br	-395	-395
OV-105	-461	-523	Carbowax 20M	-400	-387
OV-3	-458	-523	QBP Nitrate	-365	-386
OV-7	-467	-504	TBA PTS	-384	-384
OV-11	-475	-478	QBA PIC	-411	-381
QBA OS	-446	-469	QBA PTS	-377	-377
OV-17	-470	-463	QBA BS	-382	-377
QBP CHES	-442	-462	QBA FBS	-409	-361
TBMA OS	-426	-459	QBA MOPSO	-385	-361
QBP Cl	-411	-456	QBA BES	-345	-338
QBP PTS	-464	-452	QF-1	-390	-336
OV-22	-458	-439	QBA ACES	-319	-312
QBA CAPS	-421	-437	QBP I	-375	-281
PPE-5	-487	-436	QBP TAPSO	-299	-278
QBA BuS	-403	-432	QBA TAPS	-308	-277
QBA CHES	-413	-431	DEGS	-324	-275
QBP MOPS	-419	-429	TCEP	-291	-289
THPED	-414	-425	QEA PTS	-286	-267
TBMA HS	-400	-423	QBA TAPSO	-274	-260
QBA HS	-410	-422	OV-275	-279	-255
OV-225	-418	-410			

To standardize the solvent strength scale the free energy per methylene group has been expressed per unit solvent volume<sup>27</sup>. The choice of standard state for the solvent is dictated largely by practical considerations. However, a brief perusal of the data in Table IV indicates that the solvent strength parameter scale is more in keeping with chemical intuition than the free energy scale itself. For example, there is a linear increase in polarity with increasing mole percent of phenyl groups for the poly(methylphenylsiloxanes) while there is no defined trend for the free energy scale<sup>27</sup>. For the homologous series of tetra-*n*-butylammonium alkanesulfonate and perfluoroalkanesulfonate salts there is a linear change for the solvent strength parameter with increasing sulfonate chain length which, again, is not observed for the partial molar Gibbs free energy of solution for a methylene group<sup>50,74</sup>. Highly fluorinated phases are likely to behave anomalously on both polarity scales due to the unusually weak dispersive interactions of the fluorocarbon portion of the molecule with a methylene group<sup>50,52,74</sup>. Thus, for example, the positioning of QF-1 among phases in Table IV that intuition predicts should be more polar.

Another strange feature is the location of the liquid organic salts on both scales. The salts are distributed throughout both scales with those containing cations and/or anions with greater numbers of methylene groups being the least polar. The solubility of a methylene group seems to depend primarily on the size and nature of the individual ions and is influenced to a much lesser extent by the coulombic fields existing between ions. Given the strong selective interactions of these salts with polar solutes, discussed in the next section, their potential for polar interactions may be misrepresented by their relative position in Table IV. These features only serve to emphasize the difficulties and inadequacies of defining a single parameter scale for a general term like solvent strength and it seems inevitable that anomalies and exceptions will arise.

#### *General thermodynamic scales of solvent selectivity*

The solvent selectivity of a stationary phase is defined here as the capacity of the phase to enter into specific intermolecular interactions expressed by the Gibbs free energy of solution (formally equivalent to the chemical potential) for a number of test solutes selected to emphasize the magnitude of the intended interaction. A sufficient number of test solutes are required to adequately characterize the principal intermolecular interactions of dispersion, induction, orientation and donor-acceptor complexation. Unfortunately no solute interacts by a single mechanism except for the limited case of the solution of one alkane in another. For all other cases multiple interactions are involved. Test solutes, therefore, must be selected carefully to express a dominant single interaction with lesser contributions from other possible concurrent interactions. An additional constraint is the volatility characteristics of the test solutes which must permit the convenient determination of retention on a wide range of liquid phases at a common temperature. With these considerations in mind *n*-butylbenzene, octanol, nitrobenzene and benzodioxan were selected as test solutes from a candidate list of 34 possible test solutes, representing a wide range of compound types, with all measurements being made at 121°C<sup>27</sup>. The molar standard state was selected for the solvent and the magnitude of solute-solvent interactions were determined by the partial molar Gibbs free energy of solution for each test solute.

*n*-Butylbenzene was selected as a test solute to complement information

TABLE V

## PARTIAL MOLAL GIBBS FREE ENERGY OF SOLUTION FOR BUTYLBENZENE AT 121°C

Stationary phase	Free energy (cal/mol)	Stationary phase	Free energy (cal/mol)
OV-275	-3105 ± 97	SE-30	-4460 ± 81
QBA TAPSO	-3356 ± 66	OV-105	-4486 ± 46
QEA PTS	-3449 ± 34	TBMA OS	-4494 ± 63
QBA ACES	-3650 ± 33	OV-25	-4495 ± 13
DEGS	-3706 ± 51	OV-22	-4515 ± 22
TCEP	-3764 ± 27	OV-330	-4564 ± 13
QF-1	-3768 ± 29	OV-3	-4579 ± 26
QBA MOPS	-4187 ± 24	OV-17	-4597 ± 30
THPED	-4191 ± 32	QBA OS	-4608 ± 23
QBA MS	-4265 ± 48	OV-11	-4619 ± 48
QBA MOPS	-4275 ± 49	OV-7	-4620 ± 44
QBA PTS	-4293 ± 28	PPE-5	-4838 ± 24
OV-225	-4300 ± 44	DEHPA	-4920 ± 29
TBA PTS	-4302 ± 26	Apolane-87	-4995 ± 19
QBA BuS	-4306 ± 63	DEHP	-5011 ± 12
Carbowax 20M	-4394 ± 9	Squalane	-5140 ± 34
QBA PIC	-4424 ± 12	DDP	-5173 ± 26

contained in the partial molar Gibbs free energy of solution for a methylene group scale (since this value is based on the difference in retention of two test solutes the standard state for the liquid is unimportant and the numerical value is identical for a molar or molal solvent standard state). The methylene group scale should be a reasonable scale of dispersive interactions while the retention of *n*-butylbenzene should depend largely on dispersive interactions but because of its greater polarizability it would be expected to exhibit stronger inductive interactions in the presence of a dipole and to exhibit some weak proton-acceptor capacity. Experimental values

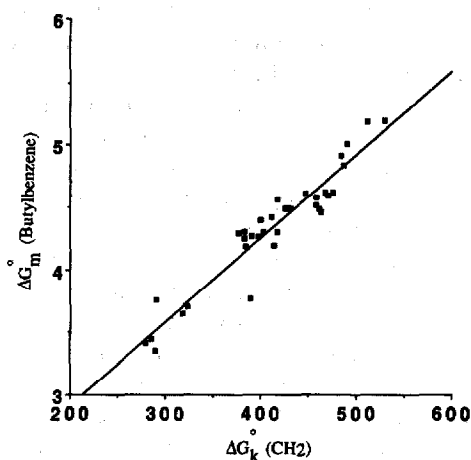


Fig. 2. Plot of the partial molar Gibbs free energy of solution for butylbenzene against the partial molar Gibbs free energy of solution for a methylene group for the 34 phases identified in Table V.

for the partial molal Gibbs free energy of solution for *n*-butylbenzene in a wide range of liquid phases are summarized in Table V. If these values are plotted against the partial molal Gibbs free energy of solution for a methylene group for the same phases (Fig. 2), a good correlation is found between the two scales ( $r = 0.96$ ,  $n = 34$ ). There is no obvious trend in the data to suggest increasing solute solubility as the dipole character or proton donor capacity of the liquid phase increases. The phase with the largest deviation from the line drawn through the experimental data is the fluorocarbon-containing phase QF-1, which might well show exceptional behavior due to the weak dispersive interactions and strong polarizing effects of the fluorocarbon groups. In other cases it is not sensible to attempt a distinction between any weak selective interactions from those of the experimental uncertainty in the data. It can be concluded that no additional information is contained in the scale based on *n*-butylbenzene that is not available from the free energy of solution for a methylene group. It could be argued that *n*-butylbenzene is not a particularly responsive probe for inductive interactions. The average molecular polarizability of benzene is about half that of biphenyl and diphenyl-ether and about two-thirds that of naphthalene<sup>75</sup>. Thus, a more polarizable probe than *n*-butylbenzene might be a better indicator of inductive interactions. A counter argument could be that there is a tendency to underestimate the importance of inductive interactions for the retention of non-polar solutes in polar solvents as was pointed out by Meyer *et al.*<sup>76</sup>. Consequently, if the inductive contribution is already folded into the methylene group free energy scale then parallel agreement between the two scales would be predicted. It should be pointed out that much of the available literature data on the respective solubility (retention) of *n*-alkanes and aromatic solutes is not useful for extending the results of the above study as it is, generally, uncorrected for the influence of interfacial adsorption. On polar phases interfacial adsorption may be the dominant retention mechanism for hydrocarbons while aromatic compounds show a greater preference for partitioning. In this case the general elution order does not necessarily reflect the solution behavior of the solutes.

Nitrobenzene was selected as the test solute to characterize dipole interactions with some weak proton acceptor capacity<sup>27</sup>. The experimental data for the partial molal Gibbs free energy of solution for nitrobenzene are summarized in Table VI. A plot of the partial molal Gibbs free energy of solution for nitrobenzene against the partial molal Gibbs free energy of solution for a methylene group takes the form of a scatter plot (Fig. 3), confirming that the retention of nitrobenzene cannot be explained from dispersive interactions alone. The magnitude of the free energy scale for nitrobenzene, Table VI, stretching from about 4300 to 6700 cal/mol provides a good separation of the phases with respect to the assessment of their capacity for orientation interactions. The strongest interactions are shown by the ionic phases as a group indicating the strong dipole interactions possible with the coulombic field between the ions. These interactions are always strong and not greatly influenced by the identity of the ions. The weakest interactions being associated with salts containing anions capable of intermolecular hydrogen bonding interactions that modify the spacing between ions and subsequently their coulombic interactions<sup>42</sup>. Of the non-ionic phases Carbowax 20M shows the strongest interaction with nitrobenzene followed by TCEP, DDP and PPE-5. The latter two phases do not have large dipole moments and their ranking might well be due to selective charge transfer interactions with nitrobenzene. Commonly accepted polar phases such as DEGS, OV-275 and

TABLE VI

PARTIAL MOLAL GIBBS FREE ENERGY OF SOLUTION FOR NITROBENZENE AT 121°C

<i>Stationary phase</i>	<i>Free energy (cal/mol)</i>	<i>Stationary phase</i>	<i>Free energy (cal/mol)</i>
Apolane-87	-4343 ± 21	PPE-5	-5711 ± 26
Squalane	-4416 ± 26	DDP	-5778 ± 19
SE-30	-4519 ± 69	TCEP	-5806 ± 6
OV-105	-4755 ± 46	QBA ACES	-5907 ± 9
OV-3	-4812 ± 38	Carbowax 20M	-5912 ± 33
QF-1	-4833 ± 23	TBA PTS	-6027 ± 24
OV-7	-4984 ± 45	TBMA OS	-6042 ± 26
OV-11	-5114 ± 45	QBA PIC	-6046 ± 16
OV-25	-5172 ± 25	QBA MOPSO	-6102 ± 22
OV-17	-5179 ± 29	QBP I	-6107 ± 9
OV-22	-5181 ± 22	QBA BuS	-6109 ± 32
OV-275	-5254 ± 41	QBP CHES	-6165 ± 29
OV-225	-5494 ± 16	QBA OS	-6171 ± 45
QBP TAPSO	-5534 ± 2	QBA MS	-6206 ± 52
DEGS	-5549 ± 59	QBA MOPS	-6206 ± 9
DEHPA	-5561 ± 12	QBA PTS	-6232 ± 28
QBA TAPSO	-5573 ± 2	QBP MOPS	-6246 ± 53
THPED	-5622 ± 21	QBP Nitrate	-6289 ± 19
QBA BES	-5666 ± 67	QBP Br	-6369 ± 12
OV-330	-5672 ± 8	QBP Cl	-6405 ± 51
QEA PTS	-5701 ± 22	QBP PTS	-6714 ± 38

OV-225 occupy intermediate positions in Table VI. The dipole interactions for OV-275 are only moderate and it can be seen from comparing data in Table IV and V that its status as a polar phase probably has just as much to do with its very weak interactions with the non-polar portion of solutes (weak dispersive interactions) as its capacity for

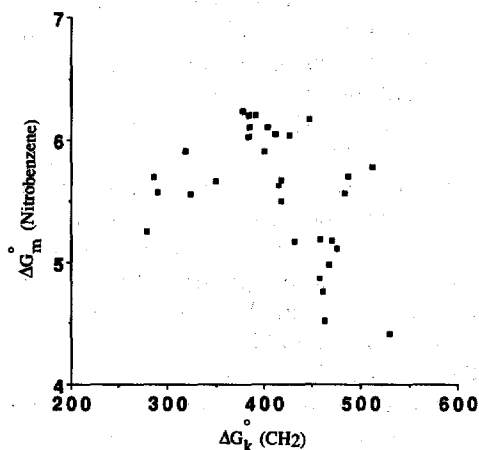


Fig. 3. Plot of the partial molal Gibbs free energy of solution for nitrobenzene against the partial molal Gibbs free energy of solution for a methylene group for the 31 phases identified in Table VI.

TABLE VII

PARTIAL MOLAL GIBBS FREE ENERGY OF SOLUTION FOR OCTANOL AT 121°C

<i>Stationary phase</i>	<i>Free energy (cal/mol)</i>	<i>Stationary phase</i>	<i>Free energy (cal/mol)</i>
OV-275	-3865 ± 77	PPE-5	-4931 ± 28
QF-1	-3987 ± 26	QBA TAPSO	-5018 ± 5
OV-25	-4381 ± 26	DDP	-5051 ± 22
Apolanc-87	-4405 ± 1	QBA PIC	-5174 ± 21
OV-22	-4469 ± 60	OV-330	-5196 ± 31
SE-30	-4477 ± 53	Carbowax 20M	-5221 ± 15
DEGS	-4540 ± 44	THPED	-5240 ± 12
OV-17	-4602 ± 31	QEA PTS	-5233 ± 23
OV-3	-4605 ± 50	QBA BES	-5477 ± 66
OV-105	-4607 ± 42	QBA MOPSO	-5610 ± 32
TCEP	-4609 ± 10	QBA ACES	-5735 ± 46
Squalane	-4623 ± 28	TBA PTS	-5883 ± 6
OV-11	-4629 ± 38	QBA MOPS	-6051 ± 26
OV-7	-4641 ± 55	QBA PTS	-6314 ± 28
OV-225	-4769 ± 34	QBA MS	-6366 ± 13

strong polar interactions with functional groups. This is probably accounted for by the helical structure of the polymer favoring strong intramolecular interactions between the cyano groups. The properties of OV-225, which contains fewer cyano groups than OV-275 but shows a stronger interaction with nitrobenzene, can probably be explained by the greater disruption of the helical structure of the polymer by the more bulky substituent groups serving to diminish the extent of intramolecular interactions between the cyano groups thus increasing the capacity of the phase for solute interactions.

Octanol was selected as the test solute for solvent proton acceptor capacity with some weak dipole and proton donor (solvent) capability. The experimental data for the partial molal Gibbs free energy of solution for octanol are summarized in Table VII. Plots of the partial molal Gibbs free energy of solution for *n*-octanol against the equivalent values for nitrobenzene or the partial molar Gibbs free energy of solution for a methylene group form scatter plots in keeping with the hypothesis that the dominant solution interaction for *n*-octanol is the capacity of the solvent for proton acceptor interactions. The magnitude of the free energy scale for octanol (Table VI), stretching from about 3800 to 6400 cal/mol provides a good separation of the phases with respect to the assessment of their capacity for proton acceptor interactions. The strongest interactions are again shown by the liquid organic salts, but unlike the results for nitrobenzene, the identity of the anion is important. At present there is no independent scale of anion basicity for the liquid organic salts to compare with the data in Table VII. But it seems reasonable to identify the basicity of the anion as the dominant factor in controlling the retention of proton donor solutes<sup>77,78</sup>. Of the non-ionic phases the strongest interactions are shown by Carbowax 20M, OV-330, THPED and DDP but these are quite weak compared to the strongest interactions shown by the liquid organic salts. The weakest interactions are shown by OV-275 and QF-1 which can probably be accounted for by the weak dispersive interactions of these

TABLE VIII

PARTIAL MOLAL GIBBS FREE ENERGY OF SOLUTION FOR BENZODIOXAN AT 121°C

<i>Stationary phase</i>	<i>Free energy (cal/mol)</i>	<i>Stationary phase</i>	<i>Free energy (cal/mol)</i>
QF-1	-4571 ± 17	THPED	-5745 ± 3
SE-30	-4866 ± 83	QEA PTS	-5787 ± 17
OV-105	-5010 ± 70	DEGS	-5835 ± 58
OV-3	-5149 ± 33	QBA ACES	-5876 ± 18
OV-275	-5302 ± 44	TCEP	-5954 ± 9
OV-7	-5330 ± 44	OV-330	-5968 ± 4
Apolane-87	-5374 ± 17	QBA PIC	-6006 ± 12
Squalane	-5444 ± 30	TBA PTS	-6040 ± 27
OV-11	-5481 ± 41	DDP	-6043 ± 22
QBA TAPSO	-5556 ± 170	PPE-5	-6059 ± 32
OV-17	-5560 ± 33	QBA MOPSO	-6072 ± 6
OV-22	-5560 ± 23	QBA MOPS	-6167 ± 10
OV-225	-5601 ± 103	QBA MS	-6169 ± 51
OV-25	-5628 ± 22	Carbowax 20M	-6182 ± 22
QBA BES	-5646 ± 90	QBA PTS	-6202 ± 24

phases with the alkyl chain of octanol and the lack of significant solvent proton acceptor capability. These are then followed by a large group of phases having a narrow range of free energy values indicating that many of the common phases currently employed in gas chromatography do not have significant proton acceptor capacity. At first sight the relative position of squalane in Table VII might seem to be anomalous but this is probably a consequence of the clustering of phases lacking significant proton acceptor capacity into the first portion of the table combined with the strong dispersive interaction of squalane with the alkyl chain of octanol.

Benzodioxan was selected as the test solute for solvent proton donor capacity with some weak orientation capability. The experimental data for the partial molal Gibbs free energy of solution for benzodioxan are summarized in Table VIII. When

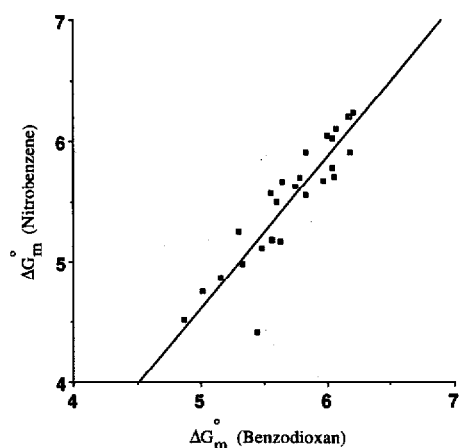


Fig. 4. Plot of the partial molal Gibbs free energy of solution for nitrobenzene against the partial molal Gibbs free energy of solution for benzodioxan for 25 of the phases in common to Table V and Table VIII.



plotted against the partial molal Gibbs free energy of solution for nitrobenzene (Fig. 4), there is a reasonable correlation between the two data sets ( $r = 0.91$ ,  $n = 25$ ). Also, those phases containing hydroxyl groups, which might be anticipated to show the strongest proton donor capacity, THPED, QBA BES and QBA TAPSO, etc. are bracketed by phases in Table VIII that clearly lack proton donor groups in their structure. It must be concluded, therefore, that the selective interactions of benzodioxan are governed by orientation interactions and as a test solute to probe solvent proton donor capacity it is unacceptable.

There are several practical problems in the selection of a test solute to replace benzodioxan. Nitrogen-containing heterocyclic bases such as pyridine, morpholine, methylimidazole, quinoline, anilines, etc. are difficult to elute with acceptable peak shape or with complete mass recovery from non-polar phases and the liquid organic salts. For the non-polar phases undoubtedly the problem is due to solute interactions with the residual silanol groups of the support that remain even after exhaustive silanization. For the liquid organic salts chemical as well as strong physical interactions may be involved<sup>51</sup>. Oxygen-containing heterocyclic compounds tend to mimic the behavior of benzodioxan<sup>27</sup>. Sulfoxides and phosphine oxides exhibit poor peak shapes on many phases. Dibutylformamide shows reasonable peak shapes and retention on moderately polar and polar phases; it is difficult to prevent the formation of tailing peaks on non-polar phases. The partial molal Gibbs free energy of solution for dibutylformamide on a limited number of polar and proton donor phases is summarized in Table IX. When plotted against the partial molal Gibbs free energy of solution for nitrobenzene a scatter plot is obtained, unlike benzodioxan, indicating that orientation is not the dominant mechanism for the selective retention of dibutylformamide. Similar results were found when the partial molal Gibbs free energy of solution for dibutylformamide was plotted against the partial molar Gibbs free energy of solution for a methylene group. Also encouraging from Table IX is the observation that dibutylformamide interacts most strongly with THPED and QBA MOPSO, phases that contain hydroxyl groups. Although only preliminary data are available, dibutylformamide is a promising test solute for assessing solvent proton donor capacity.

## CONCLUSIONS

The framework presented in this paper is useful for assessing the solvent strength and selectivity of liquid phases used in gas chromatography. Solvent strength is easily

TABLE IX

PARTIAL MOLAL GIBBS FREE ENERGY OF SOLUTION FOR DIBUTYLFORMAMIDE AT 121°C

<i>Stationary phase</i>	<i>Free energy (cal/mol)</i>	<i>Stationary phase</i>	<i>Free energy (cal/mol)</i>
THPED	-6835 ± 78	OV-17	-5975 ± 22
QBA MOPSO	-6410 ± 29	Carbowax 20M	-5895 ± 54
QBA MOPS	-6400 ± 19	OV-275	-5704 ± 64
TCEP	-6278 ± 48	OV-225	-5601 ± 35

understood but much more difficult to reduce to an experimentally determined parameter. The solvent strength parameter described here provides a scale which agrees empirically with chemical intuition for non-ionic phases. Ionic phases and those containing perfluorocarbon chains may not be correctly positioned on the scale with respect to the other phases. Nitrobenzene and octanol are satisfactory test solutes for solvent dipole and proton acceptor interactions, respectively. Benzodioxan is not a suitable test solute for solvent proton donor capacity and will need to be replaced. Dibutylformamide was identified as a possible candidate to replace benzodioxan but further work will be needed to establish this. The scales of partial molar Gibbs free energy of solution for a methylene group and the partial molal Gibbs free energy of solution for butylbenzene provide duplicate information and if a test solute susceptible to inductive interactions is desired then *n*-butylbenzene should be replaced with a different, as yet unidentified, test solute.

From the data presented it is obvious that there is plenty of scope for the development of new selective stationary phases for gas chromatography. Many of the common phases in current use span quite a narrow range of solvent properties. In this respect it is gratifying to see that the liquid organic salt phases extend the range of orientation and solvent proton acceptor interactions beyond those of the non-ionic phases that dominate the contemporary practice of gas chromatography. It also seems likely that there is a need for new strong proton donor phases, although proof of this must wait the development of an acceptable method of assessing solvent proton donor capacity.

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#### REFERENCES

- 1 C. F. Poole and S. K. Poole, *Anal. Chim. Acta*, 216 (1989) 109.
- 2 C. F. Poole and S. A. Schuette, *Contemporary Practice of Chromatography*, Elsevier, Amsterdam, 1984, p. 42.
- 3 C. F. Poole and S. K. Poole, *Chem. Rev.*, 89 (1989) 377.
- 4 E. sz. Kovats, *Chimica*, 22 (1968) 459.
- 5 L. Rohrschneider, *Fresenius' Z. Anal. Chem.*, 170 (1959) 256.
- 6 E. Bayer, *Angew. Chem.*, 71 (1959) 299.
- 7 G. Schomburg, *J. Chromatogr.*, 14 (1964) 157.
- 8 R. S. Lowry, H. B. Woodruff and T. L. Isenhour, *J. Chromatogr. Sci.*, 14 (1976) 1929.
- 9 A. Voelkel, *J. Chromatogr.*, 457 (1988) 73.
- 10 A. Voelkel, J. Szymanowski, J. Berger and K. Ebert, *J. Chromatogr.*, 398 (1987) 31.
- 11 L. R. Snyder, *J. Chromatogr. Sci.*, 16 (1978) 223.
- 12 M. Roth and J. Novak, *J. Chromatogr.*, 234 (1982) 337.

- 13 A. Voelkel, *J. Chromatogr.*, 435 (1988) 29.
- 14 W. A. Aue and V. Paramasigamani, *J. Chromatogr.*, 116 (1978) 253.
- 15 C. F. Poole, S. K. Poole, R. M. Pomaville and B. R. Kersten, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 10 (1987) 670.
- 16 R. M. Pomaville and C. F. Poole, *Anal. Chem.*, 60 (1988) 1103.
- 17 B. R. Kersten and C. F. Poole, *J. Chromatogr.*, 452 (1988) 191.
- 18 J. Sevcik and M. S. H. Lowentap, *J. Chromatogr.*, 217 (1981) 139.
- 19 P. Chovin and J. Lebbe, *J. Gas Chromatogr.*, 4 (1966) 37.
- 20 E. sz. Kovats and P. B. Weisz, *Ber. Bunsenges. Phys. Chem.*, 69 (1965) 813.
- 21 R. C. Castells, *J. Chromatogr.*, 350 (1985) 339.
- 22 J. Novak, J. Ruzickova, S. Wicar and J. Janak, *Anal. Chem.*, 45 (1973) 1365.
- 23 R. V. Golovnya and T. A. Misharina, *J. High Resolut. Chromatogr.*, 3 (1980) 51.
- 24 C. F. Poole, K. G. Furton, R. M. Pomaville, S. K. Poole and B. R. Kersten, in R. J. Gale and D. G. Lovering (Editors), *Molten Salt Techniques*, Plenum, New York, Vol. 4, 1990, in press.
- 25 K. G. Furton and C. F. Poole, *J. Chromatogr.*, 399 (1987) 47.
- 26 B. R. Kersten, C. F. Poole and K. G. Furton, *J. Chromatogr.*, 411 (1987) 43.
- 27 B. R. Kersten, S. K. Poole and C. F. Poole, *J. Chromatogr.*, 468 (1989) 235.
- 28 S. K. Poole, B. R. Kersten, R. M. Pomaville and C. F. Poole, *LC · GC, Mag. Liq. Gas Chromtogr.*, 6 (1988) 400.
- 29 W. R. McReynolds, *J. Chromatogr. Sci.*, 8 (1970) 685.
- 30 J. A. Yancey, *J. Chromatogr. Sci.*, 24 (1986) 117.
- 31 L. Rohrschneider, *Adv. Chromatogr.*, 4 (1967) 333.
- 32 L. Rohrschneider, *J. Chromatogr. Sci.*, 11 (1973) 160.
- 33 P. S. H. Na and L. B. Rogers, *J. Chromatogr.*, 329 (1985) 5.
- 34 S. D. West, *J. Chromatogr. Sci.*, 27 (1989) 2.
- 35 M. B. Evans, J. K. Haken and T. Toth, *J. Chromatogr.*, 351 (1986) 155.
- 36 M. B. Evans and J. K. Haken, *J. Chromatogr.*, 389 (1986) 15.
- 37 M. B. Evans and J. K. Haken, *J. Chromatogr.*, 406 (1987) 105.
- 38 E. Chong, B. de Bricero, G. Miller and S. J. Hawkes, *Chromatographia*, 20 (1985) 293.
- 39 E. Fernandez-Sanchez, A. Fernandez-Torres, J. A. Garcia-Dominguez, J. M. Santiuste and E. Pertierra-Rimda, *J. Chromatogr.*, 457 (1988) 55.
- 40 B. L. Karger, L. R. Snyder and C. Eon, *Anal. Chem.*, 50 (1978) 2126.
- 41 J. E. Brady, D. Bjorkman, C. D. Herter and P. W. Carr, *Anal. Chem.*, 56 (1984) 278.
- 42 S. K. Poole, P. H. Shetty and C. F. Poole, *Anal. Chim. Acta*, 218 (1989) 241.
- 43 T. H. Risby, P. C. Jurs and B. L. Reinbold, *J. Chromatogr.*, 99 (1974) 173.
- 44 R. L. Reinbold and T. H. Risby, *J. Chromatogr. Sci.*, 13 (1975) 372.
- 45 C. E. Figgins, T. H. Risby and P. C. Jurs, *J. Chromatogr. Sci.*, 14 (1976) 453.
- 46 S. K. Poole, B. R. Kersten and C. F. Poole, *J. Chromatogr.*, 471 (1989) 91.
- 47 C. F. Poole, R. M. Pomaville and T. A. Dean, *Anal. Chim. Acta*, 225 (1989) 193.
- 48 R. M. Pomaville, S. K. Poole, L. J. Davis and C. F. Poole, *J. Chromatogr.*, 433 (1988) 1.
- 49 B. R. Kersten and C. F. Poole, *J. Chromatogr.*, 399 (1987) 1.
- 50 R. M. Pomaville and C. F. Poole, *J. Chromatogr.*, 468 (1989) 261.
- 51 S. K. Poole and C. F. Poole, *J. Chromatogr.*, 435 (1988) 17.
- 52 R. M. Pomaville and C. F. Poole, *Anal. Chim. Acta*, 200 (1987) 151.
- 53 R. L. Martin, *Anal. Chem.*, 33 (1961) 347.
- 54 D. E. Martire, in J. H. Purnell (Editor), *Progress in Gas Chromatography*, Wiley, New York, 1968, p. 93.
- 55 V. G. Berezkin, *J. Chromatogr.*, 159 (1978) 359.
- 56 H.-L. Liao and D. E. Martire, *Anal. Chem.*, 44 (1972) 498.
- 57 D. F. Fritz, A. Sahli and E. sz. Kovats, *J. Chromatogr.*, 186 (1979) 63.
- 58 R. N. Nikolov, *J. Chromatogr.*, 241 (1982) 237.
- 59 O. Wicarova, J. Novak and J. Janak, *J. Chromatogr.*, 51 (1970) 3.
- 60 R. J. Laub, J. H. Purnell, P. S. Williams, M. W. P. Harbison and D. E. Martire, *J. Chromatogr.*, 155 (1978) 233.
- 61 J. Q. Walker, S. F. Spencer and S. M. Sonchik, *J. Chromatogr. Sci.*, 24 (1985) 555.
- 62 E. Fernandez-Sanchez, J. A. G. Dominguez, J. G. Munoz and M. L. Molera, *J. Chromatogr.*, 299 (1984) 151.
- 63 G. Korosi and E. sz. Kovats, *J. Chem. Eng. Data*, 26 (1981) 323.

- 64 D. F. Cadogen, J. R. Conder and J. H. Purnell, *J. Phys. Chem.*, 73 (1969) 708.
- 65 J. R. Conder, D. C. Locke and J. H. Purnell, *J. Phys. Chem.*, 73 (1969) 700.
- 66 A. N. Korol, *J. Chromatogr.*, 67 (1972) 213.
- 67 J. Serpinet, *Anal. Chem.*, 48 (1976) 2264.
- 68 S. Moriguchi and S. Takei, *J. Chromatogr.*, 350 (1985) 15.
- 69 J. R. Conder and C. L. Young, *Physicochemical Measurements by Gas Chromatography*, Wiley, New York, 1979, p. 315.
- 70 R. J. Laub, *Anal. Chem.*, 56 (1984) 2215.
- 71 R. V. Golovnya, *J. Chromatogr.*, 364 (1986) 193.
- 72 R. V. Golovnya and D. N. Grigoryeva, *Chromatographia*, 17 (1983) 613.
- 73 S. J. Hawkes, *Chromatographia*, 25 (1988) 313.
- 74 R. M. Pomaville and C. F. Poole, 499 (1990) 749.
- 75 M. L. Lee, J. C. Kuei, N. W. Adams, B. J. Tarbet, M. Nishioka, B. A. Jones and J. S. Bradshaw, *J. Chromatogr.*, 302 (1984) 303.
- 76 E. F. Meyer, K. S. Stec and R. D. Hotz, *J. Phys. Chem.*, 77 (1973) 2140.
- 77 C. F. Poole, K. G. Furton and B. R. Kersten, *J. Chromatogr. Sci.*, 24 (1986) 400.
- 78 K. G. Furton, C. F. Poole and B. R. Kersten, *Anal. Chim. Acta*, 192 (1987) 255.