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## THERMODYNAMIC APPROACH TO THE PRACTICAL CHARACTERIZATION OF SOLVENT STRENGTH AND SELECTIVITY OF COMMONLY USED STATIONARY PHASES IN GAS CHROMATOGRAPHY

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### SUMMARY

A new approach is proposed for the determination of solvent strength and solvent selectivity in gas chromatography based on thermodynamic considerations. The solvent strength is defined as the partial molar Gibbs free energy of solution for a methylene group per unit solvent volume. Solvent selectivity is determined as the partial molal Gibbs free energy of solution for the test solutes *n*-butylbenzene, 1-octanol, benzodioxan and nitrobenzene. Solvent strength and selectivity values are provided for 24 commonly used liquid phases spanning a wide range of solvent properties.

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### INTRODUCTION

Chromatographers are frequently faced with the problem of having to select a stationary phase to perform a given separation. In some cases an earlier report in the literature indicating the separation of the same or of a similar sample will provide a solution. In many cases, however, it is more likely that an empirical choice will have to be made or the recommended phase from the literature source is unavailable. If the composition of the sample is known then a stationary phase with complementary selectivity would be a reasonable first choice and if the solvent selectivity of all of the most frequently encountered phases was known then a better selection could be made and redundant phases with similar properties identified for replacement. Stocking many phases with similar properties in the laboratory could be avoided and when a phase not on hand was required for a particular analysis, perhaps following a suggestion from a literature source, the nearest chemical equivalent phase could be substituted with reasonable expectations of obtaining a similar separation. To achieve this goal we need a reasonable model of the way solutes of different kinds interact with common stationary phases in such a way that these phases can be ranked in a quantitative manner by their capacity to enter into specific intermolecular interactions. Unfortunately fundamental approaches have not advanced to the point where an exact model can be put forward to describe the principal intermolecular forces between complex molecules. Chromatographers have come to rely, therefore, on empirical models to estimate the solvent strength and selectivity of stationary

phases of which the Rohrschneider/McReynolds system of phase constants<sup>1-3</sup>, solubility parameters<sup>4,5</sup>, the solvent selectivity triangle of Snyder<sup>6,7</sup>, Hawkes polarity indices<sup>8</sup>, selectivity indices of Evans and Haken<sup>9</sup> and various thermodynamic approaches<sup>10,11</sup> have been most widely used. For a comprehensive review and bibliography see ref. 12. It would be no disrespect to the many workers in this field to state that the system of phase constants promulgated by Rohrschneider/McReynolds is by far the most widely used in practice. McReynolds determined phase constants for over 200 liquid phases and most new phases introduced since this compilation have been characterized using the same protocol. These same phase constants are commonly reported in the catalogs of companies manufacturing or selling stationary phases and few modern text books on chromatography omit a discussion of the use of McReynolds phase constants as an aid to stationary phase selection.

Evidence has come to light in recent years which suggests that the Rohrschneider/McReynolds phase constants may be unreliable for a combination of experimental and theoretical reasons<sup>12-19</sup>. From an experimental point of view the poor retention of some test solutes at the recommended measuring temperature and the failure to account for interfacial adsorption as a significant retention mechanism are the major problems. In fact on many common polar phases the *n*-alkane retention index standards are retained almost exclusively by interfacial adsorption while the test solutes are retained largely by partitioning or by a mixed retention mechanism. Under these circumstances the phase constants derived from retention index differences will be meaningless and subject to substantial changes for different column packings and column types. This observation applies to other methods of determining stationary phase selectivity such as those of Snyder<sup>6</sup>, Evans and Haken<sup>9</sup> and Golovnya and Misharina<sup>10</sup> which are based on the use of the retention index system. Theoretical objections are based on the proof that the phase constants are composite terms determined by the solubility of the *n*-alkane retention index standards in the compared phases as well as the magnitude of the selective interactions of the test solutes. In fact, in the majority of cases, the magnitude of the phase constants is determined almost entirely by the properties of the *n*-alkane retention index standards and a high level of correlation exists between the phase constants and various parameters describing the solubility of the *n*-alkanes in the stationary phase. This also explains why the McReynolds phase constants tend to increase monotonously with polarity rather than showing greater variation as predicted by chemical intuition and the results from analyzing test mixtures on different phases.

The keen need for some quantitative scale of stationary phase strength and selectivity has led us to seek a solution which is fundamentally sound and not based on the use of the retention index system. Following the considerations of Golovnya and Misharina<sup>10</sup> we will define the solvent strength of a stationary phase as its capacity for various intermolecular interactions, and solvent selectivity, as the relative capacity of compared solvents for a particular intermolecular interaction. The magnitude of these interactions will be determined as the partial molal Gibbs free energy of solution for a series of test solutes selected to express specific solute-solvent interactions. This paper deals with the establishment of the experimental protocol for measuring the necessary chromatographic parameters and the uncertainty associated with their determination, the selection of the solute test substances for solvent selectivity determination and the cataloging of solvent strength and selectivity values for 24

commonly used stationary phases chosen to encompass the full range of solvent strength values.

## EXPERIMENTAL

Unless otherwise stated, all chemicals and solvents were general laboratory or analytical grade in the highest purity available. The silicone polymers SE-30 [poly(dimethylsiloxane)], OV-3 [poly(dimethylmethylphenylsiloxane) containing 10 mole % of phenyl groups], OV-7 [poly(dimethylmethylphenylsiloxane) containing 20 mole % of phenyl groups], OV-11 [poly(dimethylmethylphenylsiloxane) containing 35 mole % of phenyl groups], OV-17 [poly(methylphenylsiloxane)], OV-22 [poly(phenylmethyldiphenylsiloxane) containing 65 mole % of phenyl groups], OV-25 [poly(phenylmethyldiphenylsiloxane) containing 75 mole % of phenyl groups], OV-105 [poly(cyanopropylmethyldimethylsiloxane)], OV-225 [poly(cyanopropylmethylphenylmethylsiloxane)], OV-275 [poly(dicyanoallylsiloxane)] and OV-330 [a poly(dimethylsiloxane)-Carbowax copolymer] were obtained from Ohio Valley Specialty Chemical (Marietta, OH, U.S.A.). Squalane (2,6,10,15,19,23-hexamethyl-tetracosane), QF-1 [poly(trifluoropropylmethylsiloxane)], Carbowax 20M [poly(ethylene glycol)], DEGS [poly(diethylene glycol succinate)], TCEP [1,2,3-tris(2-cyanoethoxy)propane], PPE-5 [poly(phenyl ether) with five rings], column conditioner (a mixture of silanization reagents, No. A7682) and Chromosorb W AW (40-60 or 60-80 mesh) were obtained from Anspec (Ann Arbor, MI, U.S.A.). Tributylammonium 4-toluenesulfonate (TBA pTS), tetrabutylammonium 4-toluenesulfonate (QBA pTS), tetrabutylammonium N-(2-acetamido)-2-aminoethanesulfonate (QBA ACES) and tetrabutylammonium 3-[tris(hydroxymethyl)methylamino]-2-hydroxy-1-propanesulfonate (QBA TAPSO) were prepared as described previously<sup>16,19</sup>. Tetrabutylammonium methanesulfonate (QBA MES) was obtained from Fluka (Ronkonkoma, NY, U.S.A.), tetrabutylammonium picrate (QBA PIC) from RSA Corporation (Ardley, NY, U.S.A.) and tetraethylammonium 4-toluenesulfonate (QEA pTS) from Aldrich (Milwaukee, WI, U.S.A.).

Column packings containing from 7 to 17% (w/w) of liquid phase were prepared using the rotary evaporator technique<sup>20</sup>. After coating, the damp packings were dried in a fluidized-bed drier and packed into glass columns 1.0-3.0 m × 2 mm I.D. with the aid of suction and gentle vibration. Each column was conditioned overnight at 140°C (120°C for squalane). Column packings prepared with squalane, OV-3, OV-7, OV-11, OV-17, OV-22, OV-25, OV-105, OV-225, OV-330, PPE-5, QF-1 and SE-30 were extensively on-column silanized using repeated injections of 50  $\mu$ l of column conditioner at 140-150°C (120°C for squalane). Conditioning was considered complete when symmetrical peak shapes and invariant retention times were obtained for dipolar and hydrogen bond donor-acceptor test solutes.

To determine accurate phase loadings the amount of liquid phase coated on the support was determined by Soxhlet extraction<sup>18,21</sup>. The column packing, 0.50-1.50 g  $\pm$  0.2 mg, was placed in a sintered-glass crucible previously dried to constant weight. The crucible was placed in a standard Soxhlet extractor supported by glass beads and covered with a piece of cellulose paper to prevent splashing. The Soxhlet extractor was set to cycle at 4 to 6 times per hour for 72 h using the same solvent as used for coating.

Density as a function of temperature for the liquid phases was determined over

the temperature range 60–130°C using a modified Lipkin bicapillary pycnometer described in ref. 22. The data were fitted to the general equation

$$\rho_t = A - B(t) \quad (1)$$

where  $\rho_t$  is the liquid density at temperature  $t$ (°C) and  $A$  and  $B$  are regression coefficients summarized in Table I. Due to its high viscosity, the density of SE-30 was determined with a Gay-Lussac type pycnometer (Ace Glass, Vineland, NJ, U.S.A.). The pycnometer was thermostatted in a large volume oil-bath maintained at 121.2  $\pm$  0.02°C. The experimental density was 0.8007 g ml<sup>-1</sup>.

For column evaluation a 3700 gas chromatograph (Varian Instruments, Palo Alto, CA, U.S.A.) with heated on-column injectors and a flame ionization detector was used. The column oven temperature was measured with a National Bureau of Standards (NBS)-certified mercury thermometer to  $\pm$ 0.2°C. The column pressure drop was measured with a mercury manometer to  $\pm$ 1.0 mmHg. The carrier gas, nitrogen, was adjusted to a known flow-rate of approximately 20 ml/min using a thermostatted soap-film bubble meter. Samples of 1–100  $\mu$ l of headspace vapors (usually < 10  $\mu$ l) were injected onto the column by a gas-tight syringe to approximate the conditions for infinite dilution/zero coverage. Retention data were automatically

TABLE I  
COEFFICIENTS FOR DENSITY AS A FUNCTION OF TEMPERATURE (EQN. 1)

Stationary phase	Coefficients	
	$A$	$10^4 B$
Squalane	0.8228	6.014
OV-3	1.0444	13.899
OV-7	1.0713	11.963
OV-11	1.1362	11.771
OV-17	1.1312	9.514
OV-22	1.1741	10.832
OV-25	1.2305	11.693
OV-105	1.0209	11.517
OV-225	1.1098	7.513
OV-275	1.1723	6.539
OV-330	1.1605	11.043
QF-1	1.3025	11.337
Carbowax 20M	1.1490	9.494
DEGS	1.3009	9.969
TCEP	1.1437	9.654
PPE-5	1.2212	8.553
QEA pTS	1.1665	7.756
TBA pTS	1.1024	8.320
QBA pTS	1.0898	7.397
QBA PIC	1.1608	6.854
QBA MES	1.0726	7.509
QBA ACES	1.1275	8.741
QBA TAPSO	1.1552	8.654

recorded using a SP4100 programmable computing integrator (Spectra-Physics, Santa Clara, CA, U.S.A.).

The retention of test solutes was determined as the net retention volume given by eqn. 2

$$V_N = \frac{3}{2} (t_R - t_M) F_0 \left( \frac{T_c}{T_a} \right) \left( 1 - \frac{P_w}{P_a} \right) \left( \frac{P^2 - 1}{P^3 - 1} \right) \quad (2)$$

where  $V_N$  is the net retention volume,  $t_R$  the solute retention time,  $t_M$  the column holdup 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 temperature (K),  $T_a$  the ambient temperature (K),  $P_w$  the vapor pressure of water at  $T_a$ ,  $P_a$  the ambient pressure,  $P$  the column pressure drop equal to  $P_i/P_a$  and  $P_i$  the column inlet pressure. The gas-liquid partition coefficients were calculated by linear extrapolation to infinite phase volume of plots of  $V_N^*/V_L$  vs.  $1/V_L$  based on eqn. 3<sup>7,13,18</sup>

$$\frac{V_N^*}{V_L} = K_L + (A_{GL}K_{GL} + A_{LS}K_{GLS}) \cdot \frac{1}{V_L} \quad (3)$$

where  $V_N^*$  is the net retention volume per gram of packing,  $V_L$  the volume of liquid phase per gram of packing,  $K_L$  the gas-liquid partition coefficient,  $A_{GL}$  the gas-liquid interfacial area,  $K_{GL}$  the coefficient for adsorption at the gas-liquid interface,  $A_{LS}$  the gas-support interfacial area and  $K_{GLS}$  the coefficient for adsorption at the support surface. Values for the partition coefficients of test solutes and the uncertainty in their determination are given in Table II.

The partition coefficients for the homologous series of  $n$ -alkanes and 2-alkanones were fitted to eqn. 4

$$\log K_L = C(n) + D \quad (4)$$

where  $C$  and  $D$  are coefficients obtained by linear regression and  $n$  the number of carbon atoms for the  $n$ -alkanes and the number of carbon atoms minus 2 for the 2-alkanones. The coefficients obtained by linear regression are given in Table III.

The partial molar Gibbs free energy of solution,  $\Delta G_k^0$ , for the test solutes was calculated from the gas-liquid partition coefficient,  $K_L^X$ , according to eqn. 5

$$(\Delta G_k^0 X)^P = -2.3RT_c \log K_L^X \quad (5)$$

where  $(\Delta G_k^0 X)^P$  is the partial molar Gibbs free energy of solution of solute X on phase P and  $R$  is the universal gas constant ( $1.987 \text{ cal mol}^{-1} \text{ K}^{-1}$ ). Likewise, the partial molal Gibbs free energy of solution was defined by eqn. 6

$$(\Delta G_m^0 X)^P = -2.3RT_c \log (10^3 K_L^X / RT_c \rho_c) \quad (6)$$

where  $(\Delta G_m^0 X)^P$  is the partial molal Gibbs free energy of solution for solute X on phase P and  $\rho_c$  the density of the stationary phase at the column temperature.

TABLE II

GAS-LIQUID PARTITION COEFFICIENTS FOR TEST SOLUTES AT 121.4°C (STANDARD DEVIATION IS GIVEN IN PARENTHESIS)

<i>Stationary phase</i>	<i>Test solute</i>				
	<i>Benzene</i>	<i>n-Butylbenzene</i>	<i>cis-Hydrindane</i>	<i>1-Octyne</i>	<i>1-Dodecyne</i>
Squalane	32.1 (0.9)	437.1 (7.2)	348.1 (4.9)	114.8 (1.7)	1124.1 (17.9)
SE-30	19.7 (1.3)	187.3 (9.6)	144.0 (9.3)	62.1 (2.9)	458.3 (23.7)
OV-3	24.6 (0.8)	238.1 (4.0)	169.1 (4.3)	75.1 (2.1)	563.6 (10.9)
OV-7	26.4 (0.6)	265.4 (7.5)	179.9 (5.4)	80.9 (2.4)	603.2 (16.9)
OV-11	27.4 (1.4)	284.5 (8.7)	181.2 (6.9)	82.0 (3.7)	600.2 (17.7)
OV-17	24.7 (1.1)	282.8 (5.4)	173.3 (3.3)	79.7 (1.4)	563.2 (14.4)
OV-22	27.3 (1.1)	261.5 (3.6)	157.6 (1.6)	73.7 (2.2)	454.4 (6.2)
OV-25	31.1 (1.2)	265.9 (2.2)	152.5 (0.8)	73.8 (1.7)	474.5 (8.5)
OV-105	22.8 (0.5)	212.8 (6.2)	147.3 (5.0)	67.8 (1.9)	504.1 (14.5)
OV-225	24.8 (0.8)	194.0 (5.4)	86.4 (1.4)	44.6 (0.1)	300.2 (6.5)
OV-275	13.3 (1.5)	45.3 (2.8)	17.4 (1.8)	10.2 (1.8)	19.3 (1.7)
OV-330	32.5 (1.6)	273.9 (2.3)	127.7 (2.1)	74.8 (1.9)	496.7 (5.0)
QF-1	16.4 (1.1)	112.5 (2.1)	65.8 (0.8)	28.8 (1.4)	186.0 (3.1)
Carbowax 20M	33.6 (2.3)	222.0 (1.2)	85.6 (2.0)	53.2 (2.0)	355.1 (3.1)
DEGS	21.8 (0.6)	105.3 (3.4)	33.3 (2.2)	24.3 (1.6)	122.1 (8.0)
TCEP	25.4 (0.9)	98.6 (1.7)	27.0 (1.5)	21.9 (1.1)	73.4 (1.4)
PPE-5	39.3 (0.8)	423.2 (6.6)	220.4 (3.0)	98.6 (1.2)	738.8 (11.0)
QEA pTS	18.3 (0.7)	68.9 (1.5)	16.1 (0.4)	11.3 (0.8)	62.5 (1.9)
TBA pTS	29.3 (1.1)	191.3 (3.2)	74.8 (0.9)	36.5 (2.3)	308.2 (5.9)
QBA pTS	30.6 (0.7)	187.9 (4.2)	75.5 (2.1)	38.6 (1.1)	317.8 (12.2)
QBA PIC	35.0 (3.5)	240.6 (1.9)	89.8 (2.1)	38.5 (3.7)	316.2 (5.5)
QBA MES	28.8 (2.1)	178.7 (5.5)	70.4 (3.6)	35.1 (3.4)	320.0 (13.4)
QBA ACES	20.6 (0.9)	84.8 (1.8)	31.2 (1.7)	16.5 (1.0)	94.9 (5.2)
QBA TAPSO	17.3 (1.4)	59.9 (2.5)	23.8 (0.9)	10.7 (0.8)	52.7 (1.0)

	<i>1-Butanol</i>	<i>2-Methyl-2-pentanol</i>	<i>Dodecafluoroheptanol</i>	<i>1-Octanol</i>	<i>Phenol</i>
	Squalane	18.1 (0.9)	39.1 (0.6)	33.7 (0.4)	322.4 (5.5)
SE-30	17.3 (0.9)	26.6 (1.3)	32.9 (1.6)	191.2 (6.5)	102.5 (3.8)
OV-3	22.5 (1.8)	32.6 (0.9)	41.9 (0.8)	246.3 (7.9)	148.0 (3.5)
OV-7	23.8 (0.9)	34.3 (0.8)	44.3 (1.3)	272.7 (9.5)	182.5 (7.1)
OV-11	24.1 (1.6)	33.6 (1.3)	42.4 (1.4)	288.1 (7.0)	217.0 (6.7)
OV-17	24.4 (2.0)	32.1 (1.3)	36.5 (1.2)	284.5 (5.6)	218.4 (9.1)
OV-22	22.2 (1.1)	31.0 (1.2)	36.2 (1.8)	246.5 (9.4)	239.2 (13.5)
OV-25	29.6 (2.1)	27.1 (0.4)	28.4 (1.2)	233.0 (3.0)	253.1 (3.8)
OV-105	23.3 (0.8)	33.6 (0.5)	64.3 (2.6)	248.4 (6.6)	208.3 (4.3)
OV-225	35.3 (0.6)	37.6 (1.0)	131.4 (1.9)	353.3 (7.7)	1033.0 (19.7)
OV-275	34.3 (1.0)	17.7 (1.2)	65.1 (8.2)	119.5 (5.9)	2068.5 (35.8)
OV-330	62.2 (0.8)	57.7 (0.5)	334.5 (12.6)	614.2 (12.1)	—
QF-1	19.3 (0.9)	27.6 (0.6)	71.7 (0.6)	148.7 (2.5)	104.2 (0.7)
Carbowax 20M	73.8 (1.2)	56.7 (1.0)	287.7 (3.8)	638.1 (6.2)	5267.0 (77.1)
DEGS	51.2 (1.4)	39.8 (0.9)	168.7 (6.7)	305.5 (8.6)	2718.9 (93.9)
TCEP	60.7 (0.6)	40.4 (0.9)	166.3 (4.0)	290.2 (1.9)	3281.8 (9.8)
PPE-5	35.0 (0.5)	49.6 (1.1)	50.0 (1.0)	476.5 (8.6)	514.3 (8.1)
QEA pTS	134.8 (2.2)	58.9 (2.1)	1618.2 (28.4)	672.3 (10.0)	—
TBA pTS	166.3 (4.4)	114.8 (2.6)	2221.9 (33.8)	1441.9 (5.7)	—
QBA pTS	290.2 (5.6)	166.8 (3.7)	5911.5 (109.0)	2494.7 (45.0)	—
QBA PIC	68.2 (2.6)	57.7 (3.0)	263.7 (4.2)	627.1 (8.4)	—
QBA MES	325.3 (9.7)	181.9 (7.2)	—	2744.1 (99.6)	—
QBA ACES	207.1 (3.4)	94.0 (3.0)	—	1217.5 (36.0)	—
QBA TAPSO	106.6 (3.0)	57.3 (2.5)	—	500.5 (1.7)	—

TABLE II (continued)

Stationary phase	Test solute				
	2,4,6-Trimethyl-phenol	Benzonitrile	l-Nitropropane	l-Nitropentane	Nitrobenzene
Squalane	806.9 (17.5)	168.5 (2.9)	31.3 (0.7)	123.4 (1.8)	359.7 (5.9)
SE-30	385.5 (18.8)	111.9 (5.1)	25.7 (1.7)	84.5 (4.1)	201.8 (8.9)
OV-3	569.8 (13.0)	177.0 (4.4)	38.3 (1.3)	125.3 (2.6)	320.9 (7.7)
OV-7	711.1 (19.5)	231.0 (6.4)	46.2 (1.3)	155.0 (4.5)	422.6 (12.2)
OV-11	855.5 (24.5)	291.0 (8.6)	54.6 (2.2)	179.4 (6.1)	535.4 (15.3)
OV-17	916.1 (17.1)	319.9 (6.6)	57.3 (0.9)	186.9 (3.8)	594.3 (11.1)
OV-22	922.8 (12.7)	334.7 (5.1)	57.9 (1.6)	178.8 (2.7)	611.7 (8.5)
OV-25	949.0 (17.3)	345.1 (6.7)	57.8 (3.1)	176.3 (3.5)	631.9 (9.9)
OV-105	601.5 (16.2)	170.3 (5.4)	39.6 (1.1)	129.1 (4.4)	300.0 (8.8)
OV-225	1708.6 (36.4)	512.8 (9.4)	99.4 (1.9)	298.9 (5.7)	892.1 (9.1)
OV-275	1337.2 (43.9)	445.3 (9.5)	96.1 (1.5)	179.3 (8.5)	704.7 (18.2)
OV-330	—	626.1 (3.3)	99.8 (0.7)	290.9 (2.3)	1128.0 (6.0)
QF-1	312.0 (2.0)	274.5 (2.7)	76.4 (1.2)	213.9 (3.5)	440.3 (4.6)
Carbowax 20M	5246.4 (67.5)	878.6 (40.0)	122.2 (1.9)	315.3 (1.7)	1541.5 (32.9)
DEGS	2778.0 (92.2)	614.5 (21.5)	100.6 (3.4)	225.8 (8.2)	1109.0 (41.5)
TCEP	2933.2 (15.6)	810.4 (4.5)	156.5 (2.6)	305.3 (4.7)	1338.2 (5.2)
PPE-5	2080.9 (35.5)	602.8 (9.5)	87.3 (0.8)	302.9 (3.7)	1291.0 (21.7)
QEA pTS	—	766.1 (9.7)	112.0 (2.1)	220.2 (2.5)	1223.2 (17.2)
TBA pTS	—	979.8 (17.4)	154.8 (3.8)	414.9 (2.8)	1732.2 (26.1)
QBA pTS	—	1275.7 (21.7)	194.7 (2.9)	502.6 (9.3)	2246.3 (39.6)
QBA PIC	—	1078.9 (9.2)	166.0 (0.6)	478.5 (3.7)	1910.7 (19.7)
QBA MES	—	1204.1 (40.6)	184.9 (5.6)	479.7 (15.3)	2133.9 (70.3)
QBA ACES	—	898.2 (12.1)	133.1 (1.0)	281.8 (5.9)	1515.2 (9.0)
QBA TAPSO	—	613.1 (4.5)	95.4 (1.2)	189.9 (4.6)	1017.4 (1.5)
	1,1,2,2-Tetra-chloroethane	Pyridine	2,4,6-Trimethyl-pyridine	Aniline	N-Methylaniline
Squalane	141.7 (2.0)	43.6 (1.2)	256.6 (5.0)	170.3 (4.4)	350.5 (7.4)
SE-30	75.5 (3.7)	31.3 (2.1)	122.4 (7.3)	109.5 (5.2)	178.9 (7.6)
OV-3	108.9 (2.9)	42.0 (1.8)	163.3 (4.0)	162.6 (3.2)	267.8 (5.8)
OV-7	136.1 (4.8)	50.5 (2.0)	192.0 (4.3)	207.5 (5.0)	342.4 (7.4)
OV-11	155.6 (5.2)	57.3 (3.3)	218.9 (7.0)	259.5 (6.6)	426.5 (12.0)
OV-17	163.3 (4.7)	60.8 (2.7)	228.2 (5.0)	288.9 (4.9)	471.0 (9.9)
OV-22	161.3 (2.1)	67.5 (1.1)	225.9 (4.2)	321.3 (5.7)	506.1 (4.1)
OV-25	165.7 (1.4)	68.1 (4.9)	234.0 (5.8)	348.4 (2.7)	585.9 (10.5)
OV-105	104.7 (3.0)	39.0 (1.1)	146.4 (4.8)	163.4 (4.0)	256.7 (7.1)
OV-225	222.7 (5.2)	73.9 (1.2)	194.6 (3.3)	569.0 (12.0)	711.2 (9.7)
OV-275	149.6 (4.0)	70.8 (2.6)	81.3 (3.1)	933.6 (13.6)	708.2 (18.8)
OV-330	—	89.1 (0.7)	270.0 (2.7)	938.2 (12.2)	1058.6 (12.6)
QF-1	65.8 (0.8)	46.1 (1.3)	96.1 (1.0)	146.6 (1.2)	211.5 (2.4)
Carbowax 20M	509.1 (5.4)	111.7 (1.7)	270.6 (1.3)	1687.1 (18.7)	1459.3 (20.1)
DEGS	271.0 (9.1)	134.9 (12.1)	346.6 (28.8)	1235.4 (31.9)	977.9 (37.6)
TCEP	258.5 (0.8)	125.0 (1.2)	197.7 (3.4)	1646.5 (18.3)	1271.4 (11.2)
PPE-5	291.1 (4.5)	95.7 (3.6)	426.9 (6.9)	643.2 (10.0)	1029.5 (18.1)
QEA pTS	384.4 (6.7)	—	—	—	—
TBA pTS	593.0 (14.9)	—	—	—	—
QBA pTS	1006.6 (25.1)	136.0 (3.4)	—	3880.4 (71.1)	3393.9 (36.1)
QBA PIC	328.9 (2.9)	138.3 (4.2)	272.2 (8.9)	1789.4 (6.4)	1872.6 (18.0)
QBA MES	—	128.9 (3.3)	179.5 (7.3)	4120.4 (117.9)	3512.9 (119.0)
QBA ACES	—	111.0 (2.2)	115.9 (1.3)	3112.7 (29.9)	2282.5 (29.3)
QBA TAPSO	—	98.7 (2.1)	106.7 (4.3)	1776.1 (10.1)	1308.8 (3.2)

(Continued on p. 242)

TABLE II (continued)

Stationary phase	Test solute				
	<i>N,N</i> -Dimethyl-aniline	2,6-Dimethyl-aniline	Dioxane	Anisole	Dihexyl ether
Squalane	486.9 (6.7)	697.0 (11.4)	31.4 (0.4)	150.1 (1.9)	1710.1 (27.4)
SE-30	215.2 (11.7)	315.0 (14.2)	23.1 (1.3)	80.8 (4.5)	614.0 (31.7)
OV-3	306.8 (6.3)	480.7 (10.8)	30.7 (1.4)	110.3 (1.9)	746.2 (15.0)
OV-7	376.2 (11.1)	618.6 (17.9)	35.2 (0.9)	129.9 (3.3)	785.6 (21.8)
OV-11	451.8 (13.6)	775.0 (18.8)	39.4 (1.4)	151.1 (4.9)	766.5 (22.1)
OV-17	483.7 (9.6)	857.6 (13.4)	41.9 (1.2)	159.3 (3.3)	704.4 (18.1)
OV-22	550.5 (8.4)	906.9 (11.3)	42.3 (1.1)	165.2 (3.9)	565.9 (12.2)
OV-25	535.0 (7.7)	973.8 (19.8)	42.5 (0.8)	172.2 (3.8)	527.9 (16.1)
OV-105	275.1 (8.2)	452.4 (12.5)	28.7 (0.5)	100.4 (2.9)	659.3 (19.4)
OV-225	485.6 (15.7)	1261.1 (18.4)	45.3 (0.5)	159.7 (3.5)	309.6 (9.3)
OV-275	270.3 (6.5)	1147.8 (31.2)	41.9 (0.8)	98.3 (1.3)	13.9 (2.0)
OV-330	643.7 (5.8)	1826.1 (9.1)	53.3 (1.5)	220.4 (1.3)	451.8 (4.9)
QF-1	214.8 (1.9)	352.7 (3.4)	32.1 (0.8)	78.7 (1.1)	226.2 (1.8)
Carbowax 20M	660.4 (4.7)	2536.5 (29.0)	60.6 (1.8)	248.3 (1.7)	237.0 (0.5)
DEGS	436.8 (13.4)	1816.1 (47.6)	60.6 (3.5)	174.3 (6.4)	57.9 (10.0)
TCEP	505.1 (5.9)	2335.4 (26.9)	77.5 (1.4)	191.1 (2.2)	48.8 (2.8)
PPE-5	943.1 (15.2)	1910.3 (26.7)	69.0 (1.4)	279.0 (5.8)	859.7 (13.1)
QEA pTS	—	—	40.6 (0.6)	148.6 (2.9)	60.9 (8.9)
TBA pTS	—	—	47.8 (1.0)	216.1 (3.9)	225.0 (2.6)
QBA pTS	573.8 (10.5)	3458.4 (64.2)	53.0 (1.0)	231.7 (5.0)	190.0 (4.9)
QBA PIC	873.5 (4.3)	885.8 (13.7)	68.2 (2.6)	258.2 (1.7)	234.7 (2.7)
QBA MES	550.8 (17.3)	4036.6 (128.9)	51.4 (2.0)	221.2 (6.5)	190.4 (13.8)
QBA ACES	364.6 (4.4)	2797.2 (26.9)	44.6 (0.9)	155.3 (1.7)	43.2 (3.1)
QBA TAPSO	294.1 (1.1)	1790.7 (15.8)	38.3 (1.9)	119.8 (2.4)	37.7 (2.3)
<hr/>					
	<i>Benzodioxan</i>	<i>Nonanal</i>			
Squalane	637.6 (11.8)	424.2 (6.6)			
SE-30	314.5 (16.6)	228.2 (10.6)			
OV-3	493.3 (10.5)	303.8 (6.4)			
OV-7	658.0 (18.6)	349.3 (10.9)			
OV-11	855.8 (22.3)	374.3 (11.5)			
OV-17	967.2 (20.5)	367.9 (7.2)			
OV-22	1041.9 (15.4)	324.3(4.5)			
OV-25	1130.4 (15.7)	307.4 (6.9)			
OV-105	422.1 (12.4)	292.2 (8.8)			
OV-225	1022.7 (13.5)	349.5 (5.8)			
OV-275	749.2 (21.1)	75.9 (5.9)			
OV-330	1645.9 (4.0)	383.4 (3.7)			
QF-1	313.7 (3.4)	293.7 (2.2)			
Carbowax 20M	2179.7 (30.8)	306.3 (1.8)			
DEGS	1597.2 (58.6)	162.9 (5.7)			
TCEP	1619.2 (8.3)	173.9 (3.3)			
PPE-5	2014.5 (40.7)	581.4 (11.3)			
QEA pTS	1364.2 (14.7)	101.9 (2.1)			
TBA pTS	1761.8 (30.3)	358.1 (3.9)			
QBA pTS	2163.3 (32.4)	377.8 (4.4)			
QBA PIC	1814.6 (14.4)	499.1 (5.3)			
QBA MES	2036.4 (65.6)	349.7 (12.2)			
QBA ACES	1456.0 (16.3)	82.5 (1.8)			
QBA TAPSO	994.9 (10.8)	113.1 (5.6)			



TABLE III  
COEFFICIENTS FOR EQN. 4

Stationary phase	Homologous series	Regression coefficients			Range (n)
		C	D	r <sup>2</sup>	
Squalane	Alkanes	0.2880	-0.3586	1.00	8-13
	2-Alkanones	0.2940	0.5475	1.00	2-7
SE-30	Alkanes	0.2482	-0.3448	1.00	7-12
	2-Alkanones	0.2567	0.5361	1.00	2-7
OV-3	Alkanes	0.2517	-0.3434	1.00	9-14
	2-Alkanones	0.2542	0.6682	1.00	2-7
OV-7	Alkanes	0.2554	-0.3982	1.00	9-14
	2-Alkanones	0.2589	0.6946	1.00	2-7
OV-11	Alkanes	0.2570	-0.4617	1.00	9-14
	2-Alkanones	0.2635	0.6959	1.00	2-7
OV-17	Alkanes	0.2540	-0.4853	1.00	10-15
	2-Alkanones	0.2610	0.7127	1.00	3-7
OV-22	Alkanes	0.2449	-0.4976	1.00	10-15
	2-Alkanones	0.2541	0.6987	1.00	3-7
OV-25	Alkanes	0.2391	-0.4771	1.00	11-16
	2-Alkanones	0.2391	0.7816	0.99	2-7
OV-105	Alkanes	0.2458	-0.3152	1.00	9-14
	2-Alkanones	0.2556	0.6560	1.00	2-7
OV-225	Alkanes	0.2314	-0.6529	1.00	11-16
	2-Alkanones	0.2318	0.9187	1.00	2-7
OV-275	2-Alkanones	0.1471	0.9170	1.00	3-7
OV-330	Alkanes	0.2378	-0.5334	1.00	10-15
	2-Alkanones	0.2321	0.9301	1.00	2-7
QF-1	Alkanes	0.2070	-0.3535	1.00	11-16
	2-Alkanones	0.2185	0.9768	1.00	2-7
Carbowax 20M	Alkanes	0.2217	-0.6355	1.00	11-16
	2-Alkanones	0.2220	0.9151	1.00	2-7
DEGS	Alkanes	0.1726	-0.9028	0.98	12-16
	2-Alkanones	0.1797	0.9676	1.00	2-7
TCEP	Alkanes	0.1559	-0.7517	0.98	10-16
	2-Alkanones	0.1551	1.2126	1.00	2-7
PPE-5	Alkanes	0.2671	-0.6285	1.00	8-13
	2-Alkanones	0.2702	0.8471	1.00	2-7
QEA pTS	Alkanes	0.1586	-0.9687	0.98	12-16
	2-Alkanones	0.1586	0.8961	1.00	3-7
TBA pTS	Alkanes	0.2172	-0.6023	1.00	11-16
	2-Alkanones	0.2133	1.0266	1.00	3-7
QBA pTS	Alkanes	0.2029	-0.4776	1.00	11-16
	2-Alkanones	0.2092	1.0628	0.99	2-5
QBA PIC	Alkanes	0.2193	-0.6274	1.00	11-16
	2-Alkanones	0.2282	1.1306	1.00	2-7
QBA MES	Alkanes	0.1914	-0.3616	1.00	11-16
	2-Alkanones	0.2250	0.9624	1.00	2-6
QBA ACES	Alkanes	0.1619	-0.7035	0.99	12-16
	2-Alkanones	0.1772	0.9766	1.00	2-7
QBA TAPSO	2-Alkanones	0.1607	0.9408	1.00	2-7

The difference in free energies for solute X on two compared phases is given by eqns. 7 and 8

$$\delta(\Delta G_k^0 X)_{S_0}^P = (\Delta G_k^0 X)^P - (\Delta G_k^0 X)^{S_0} \quad (7)$$

$$\delta(\Delta G_m^0 X)_{S_0}^P = (\Delta G_m^0 X)^P - (\Delta G_m^0 X)^{S_0} \quad (8)$$

where  $\delta(\Delta G_k^0 X)_{S_0}^P$  and  $\delta(\Delta G_m^0 X)_{S_0}^P$  are the difference in the partial molar and molal, respectively, Gibbs free energy of solution for solute X on stationary phase P and squalane used as a non-polar reference phase.

The partial molar Gibbs free energy of solution for a methylene group,  $\Delta G_k^0(\text{CH}_2)^P$ , was calculated according to eqn. 9

$$\Delta G_k^0(\text{CH}_2)^P = -2.3RT_c C_p \quad (9)$$

where  $\Delta G_k^0(\text{CH}_2)^P$  is the partial molar Gibbs free energy of solution for a methylene group on phase P and  $C_p$  is the linear regression coefficient from Table III for phase P. This is identical to the partial molal Gibbs free energy of solution for a methylene group. The solvent strength parameter, SSP, is defined by eqn. 10:

$$\text{SSP} = \Delta G_k^0(\text{CH}_2)^P / \rho_c \quad (10)$$

The solvent strength parameter is formally equivalent to the partial molar Gibbs free energy of solution for a methylene group per unit solvent volume.

## RESULTS AND DISCUSSION

The nature of solute-solvent interactions in gas-liquid chromatography are undoubtedly very complex and we are a long way from a fundamental understanding of the forces involved. We must, therefore, characterize these forces in an experimental manner using empirical models which of necessity will be based on a degree of chemical intuition, factual support and common sense. This was the approach taken by Rohrschneider/McReynolds that we now feel must be abandoned for the reasons discussed previously and outlined elsewhere<sup>12-19</sup>. These authors were correct in identifying solvent strength and selectivity as the most useful parameters to characterize the solvent properties of individual liquid phases but, in our opinion, chose the wrong formalism for their calculation. In this paper we will present a new protocol for stationary phase solvent characterization that is based on sound thermodynamic principles and avoids the deficiencies of earlier approaches.

The solvent strength or polarity criteria of a liquid phase is the least satisfactory measure of the properties of a liquid phase. Although most chemists have a reasonable idea of the meaning of polarity and have no difficulty in recognizing water as a polar solvent and hexane as a non-polar one, the use of the term is still subject to considerable misunderstanding. Polarity is frequently used where selectivity is meant, at other times, polarity is taken to be the sum of induction and orientation interactions only. In thermodynamic terms polarity can be defined as the capacity of a solvent for all intermolecular interactions corresponding to the partial molar Gibbs free energy of

solution. In practice, a suitable probe must be selected to determine the polarity of a liquid phase and to enable phases to be ranked in order of polarity. Since polarity is not a unique property of a molecule but a composite expression for several different interactions there is no single substance that can be defined as polar. Several empirical solutions to this problem have been suggested previously and are reviewed elsewhere<sup>12,23</sup>. We will not discuss these further.

The measure of solvent strength cannot be based on the affinity on a polar test solute for a stationary phase as it is impossible to define a test solute expressing the singular character of polarity. The only reasonable approach is to consider the reverse situation, the reluctance of a polar phase to accept a non-polar test solute<sup>10,24-29</sup>. Theoretically perfluoroalkane solvents exhibit the least polar interactions but practically the *n*-alkanes are more useful since hydrocarbon type standards are more readily available.

The partial molar or molal Gibbs free energy of solution for a methylene group is easily determined from the retention characteristics of any suitable homologous series provided a few precautions are observed. The test solutes must be retained exclusively by gas-liquid partitioning or corrected for the contribution from interfacial adsorption. Although chemical intuition would favor the use of the *n*-alkanes as test solutes in practice they are frequently retained largely or exclusively by interfacial adsorption on polar phases<sup>12-19,29</sup>. In a number of cases it is possible to calculate meaningful values for the free energies. This is far less of a problem for test solutes of intermediate polarity such as the 2-alkanones or fatty acid methyl esters. For example, Fig. 1 shows a plot of  $V_N^*/V_L$  vs.  $1/V_L$  for tridecane and 2-octanone on a number of representative phases. The relative contribution of interfacial adsorption to retention is indicated by the slopes of the plots and the contribution of partitioning by the intercept on the  $V_N^*/V_L$  axis. Partitioning is the dominant retention mechanism for 2-octanone (and other 2-alkanones) while interfacial adsorption increases in importance with polarity for tridecane. On the most polar phases interfacial adsorption is the dominant or

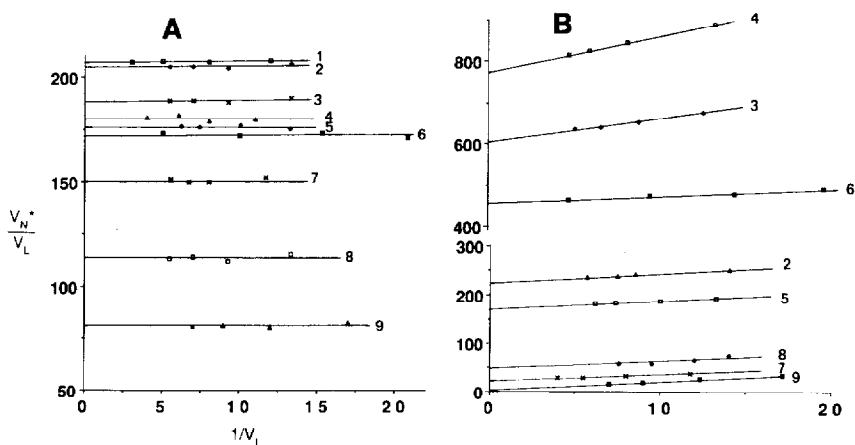


Fig. 1. Plot of  $V_N^*/V_L$  vs.  $1/V_L$  for 2-octanone (A) and tridecane (B) on the stationary phases 1 = squalane, 2 = OV-225, 3 = OV-17, 4 = OV-7, 5 = Carbowax 20M, 6 = OV-22, 7 = TCEP, 8 = DEGS and 9 = OV-275.

exclusive retention mechanism and gas-liquid partition coefficients are very small and cannot be determined with reasonable accuracy. The 2-alkanones are the preferred test solutes for determining  $\Delta G_k^0(\text{CH}_2)^p$ . Provided long chain standards are used the influence of position of the methylene group with respect to the functional group and the difference in free energy of solution for a terminal methyl group compared to a methylene group can be ignored<sup>29,30</sup>.

The partial molar Gibbs free energy of solution for a methylene group determined using *n*-alkane and 2-alkanone standards are summarized in Table IV. Where a comparison is possible the agreement is very good with an average difference between scales of 2.9% (S.D. = 3.0%). In one case, QBA MES, a difference of 13.3% was found. The reason for this are not obvious as both sets of data for the *n*-alkanes and 2-alkanones are reproducible in different experiments. Thus, it is reasonable to conclude that the choice of 2-alkanones as reference standards for determining  $C_p$  does not produce any significant bias and is preferred to the *n*-alkanes since there are some polar phases for which it is not possible to measure accurate gas-liquid partition

TABLE IV

PARTIAL MOLAR GIBBS FREE ENERGY OF SOLUTION PER METHYLENE GROUP AS A MEASURE OF SOLVENT STRENGTH

Stationary phase	$\Delta G_k^0(\text{CH}_2)^p$			SSP
	Alkanes	2-Alkanones	Difference <sup>a</sup> (%)	
Squalane	-519	-530	2.1	-728
SE-30	-447	-463	3.5	-578
OV-105	-443	-461	3.9	-523
OV-3	-454	-458	0.8	-523
OV-7	-460	-467	1.5	-504
OV-11	-463	-475	2.5	-478
OV-17	-458	-470	2.6	-463
OV-22	-441	-458	3.7	-439
PPE-5	-481	-487	1.2	-436
OV-225	-417	-418	0	-410
OV-330	-428	-418	-2.4	-407
QBA MES	-345	-398	13.3	-406
OV-25	-431	-431	0	-396
Carbowax 20M	-400	-400	0	-387
TBA pTS	-391	-384	-1.8	-384
QBA PIC	-395	-411	3.9	-381
QBA pTS	-366	-377	2.9	-377
QF-1	-373	-393	5.0	-337
QBA ACES	-292	-319	-8.5	-312
QBA TPSO	-	-290	-	-276
DEGS	-311	-324	4.0	-275
TCEP	-281	-280	0	-273
QEA pTS	-286	-286	0	-267
OV-275	-	-265	-	-243

$$^a \text{ Difference} = \frac{\Delta G_k^0(\text{CH}_2)^{\text{ketone}} - \Delta G_k^0(\text{CH}_2)^{\text{alkane}}}{\Delta G_k^0(\text{CH}_2)^{\text{ketone}}} \cdot 100.$$

coefficients with the *n*-alkane standards. For perspective in comparing the partial molar free energies of solution in Table IV an error of 0.01 in  $C_p$ , corresponding to about 3–6% for the data in Table III, would result in a difference of about 18 cal mol<sup>-1</sup> in the reported values for  $\Delta G_k^0(\text{CH}_2)^P$ . Thus, differences between phases less than about 10 cal mol<sup>-1</sup> are unlikely to be significant.

Differences in molecular size and uncertainties in the molecular weight of polydisperse phases can influence the free energy largely through the entropy contribution<sup>31,32</sup>. It is necessary to correct for these variations by defining a solvent variable that is independent of solvent molecular weight. The most convenient parameter for this purpose is unit solvent volume. This term is less satisfactory than per unit of mass but is easier to calculate from available data, eqn. 10. This solvent strength parameter, SSP, show a linear increase in polarity with increasing mole percent of phenyl groups ( $r = 0.98$ ) while  $\Delta G_k^0(\text{CH}_2)^P$  at first shows a decrease in polarity up to 35% phenyl followed by an increase at higher phenyl substitution, Fig. 2. The former behavior seems more reasonable than the latter in terms of expectations from chemical intuition. The high-molecular-weight phase SE-30, a poly(dimethylsiloxane) is ranked as being similar or more polar than several poly(methylphenylsiloxane) phases on the  $\Delta G_k^0(\text{CH}_2)^P$  scale while it is ranked second to squalane in polarity on the SSP scale and separated from the poly(methylphenylsiloxanes). Similarly, the low-molecular-weight five-ring poly(phenyl ether) PPE-5 is ranked second in polarity to squalane on the  $\Delta G_k^0(\text{CH}_2)^P$  scale and would be considered less polar than the poly(methylphenylsiloxane) phases with a low incorporation of phenyl groups, again out of keeping with the known general characteristics of these solvents. It is ranked ninth to squalane on the SSP scale flanked by phases that intuition would indicate should have similar properties. The poly(trifluoropropylmethylsiloxane) phase, QF-1, is ranked fifteenth to squalane on the  $\Delta G_k^0(\text{CH}_2)^P$  scale and seventeenth on the SSP scale. This places it among phases that intuition predicts are much more polar. Perfluorocarbon phases are likely to behave anomalously on this polarity scale due to the unusually weak dispersive interactions of the fluorocarbon portion of the molecule with a methylene group<sup>33,34</sup>.

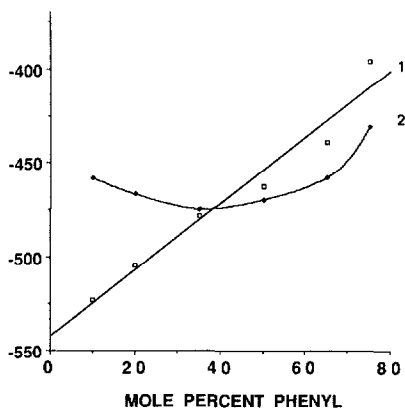


Fig. 2. Plot of the solvent strength parameter, 1, and  $\Delta G_k^0(\text{CH}_2)^P$ , 2, against the mole percent of phenyl groups for a series of poly(methylphenylsiloxane) polymers. Units for y-axis are cal · cm<sup>3</sup>/mol · g for SSP and cal/mol for  $\Delta G_k^0(\text{CH}_2)^P$ .

In conclusion, the SSP scale seems to be a more appropriate measure of solvent strength than the  $\Delta G_k^0(\text{CH}_2)^P$  scale. The 2-alkanones are suitable standards for determining the free energy of solution for a methylene group. Fluorocarbon solvents may behave anomalously on this scale. Twenty-four solvents are ranked in increasing polarity using the SSP scale in Table IV.

Whereas to define solvent strength individual solvent variations of a specific nature are ignored so as to rank solvents by a single parameter, to determine solvent selectivity it is these very differences in behavior that we attempt to quantify. There is no doubt that solvent selectivity is more important than solvent strength because it is more clearly related to the ability of individual phases to separate mixtures of similar volatility or similar polarity. To characterize the selectivity of a stationary phase a sufficient number of test solutes are required to adequately characterize the principal intermolecular interactions of dispersion, induction, orientation and donor/acceptor complexation including hydrogen bonding. Unfortunately no solutes interact by a single mechanism except for the limited case of the solution of one alkane in another and in all other cases multiple interactions are involved. The selection of test solutes involves a combination of intuition, chemical information and experiment with the additional constraint that their volatility characteristics must permit the convenient determination of retention time on a wide range of liquid phases. Interpretation will be more straight forward if retention occurs exclusively by gas-liquid partitioning. Rohrschneider chose five substances for this purpose that were later extended by McReynolds to 10 selected from a total of 68 test compounds<sup>2,3,35</sup>. Although the selection of test solutes by McReynolds seems reasonable in terms of sense (chemical intuition) the number of test solutes would seem to be excessive in terms of characterizing stationary phase selectivity. This arises because the data analysis employed by McReynolds was based on determining the number of test solutes required to accurately predict retention indices which can easily exceed the number of probes required to characterize the magnitude of solvent interactions. Applying factor analysis to the data of McReynolds indicates that the precision with which retention indices can be predicted is a stronger function of the number of test solutes employed than their character<sup>36</sup>. Hartkopf *et al.*<sup>37</sup> found that with four test solutes [benzene, nitroethane, *n*-propanol (or chloroform) and dioxane] they could reproduce Rohrschneider's data with similar precision. Lowry *et al.*<sup>38</sup> using a nearest-neighbor pattern recognition technique showed that two sets of three test solutes and several sets of four test solutes gave similar results to those obtained using the first five of the test solutes evaluated by McReynolds. In general agreement with the above studies the McReynolds test solutes benzene, *n*-butanol, 2-pentanone, 1-nitropropane and pyridine (or dioxane) have been most widely used in the contemporary scientific and trade literature for characterizing stationary phase interactions.

In practice the five solutes discussed above are not ideal solutes for investigating chromatographic interactions due to their short retention times on many phases<sup>7,13</sup>. Test solutes that are only weakly retained cannot be expected to adequately characterize stationary phase interactions and are likely to be subject to large experimental errors from small differences in retention time measurements. Some representative data for benzene, butanol, 2-pentanone, nitropropane, pyridine and dioxane on 24 phases spanning a wide polarity range are given in the form of the capacity factor for the solutes on columns containing from 12–15% (w/w) stationary

TABLE V

CAPACITY FACTOR VALUES FOR THE McREYNOLDS TEST SOLUTES AT 121.4°C ON COLUMNS CONTAINING 10–15% (w/w) OF STATIONARY PHASE

Stationary phase	Test solutes					
	Benzene	Butanol	2-Pentanone	Nitropropane	Pyridine	Dioxane
Squalane	1.97	1.25	1.66	1.94	2.72	1.97
SE-30	1.07	0.93	1.07	1.40	1.60	1.27
OV-105	1.09	1.09	1.25	1.94	1.88	1.34
OV-3	1.25	1.19	1.31	1.97	2.13	1.56
OV-7	1.27	1.12	1.36	2.21	2.48	1.67
OV-11	1.12	0.97	1.21	2.18	2.33	1.58
OV-17	0.97	0.85	1.12	2.06	2.12	1.52
OV-22	0.97	0.82	1.00	2.03	2.33	1.52
PPE-5	1.73	1.60	1.93	3.83	4.43	3.00
OV-225	1.06	1.61	1.67	4.24	3.03	1.88
OV-330	1.71	3.03	1.97	5.06	4.50	2.74
QBA MES	1.67	17.36	2.36	10.00	6.91	2.73
OV-25	0.97	0.91	1.00	1.97	2.36	1.52
Carbowax 20M	1.06	2.48	1.21	4.09	3.79	2.03
TBA pTS	1.21	6.97	1.82	6.52	—	2.27
QBA PIC	1.52	3.27	2.82	7.27	6.45	3.27
QBA pTS	1.39	13.13	2.10	8.81	6.13	2.42
QF-1	0.67	0.73	1.60	3.00	1.77	1.27
QBA ACES	0.85	8.27	1.30	5.30	4.48	1.76
QBA TAPSO	0.70	3.94	1.00	3.58	3.73	1.45
DEGS	0.76	1.76	1.06	3.42	4.85	1.97
TCEP	1.14	2.75	2.07	7.04	5.64	3.46
QEA pTS	0.81	6.05	1.03	5.06	—	1.77
OV-275	0.67	1.36	1.06	3.85	2.82	1.67

phase in Table V. The gas holdup time for these columns is typically about 0.35 min and very few solutes, therefore, have reasonable experimental retention times. For this reason and to permit phase properties to be determined at temperatures greater than 120°C Vernon *et al.* have suggested that *n*-butylbenzene, benzyl alcohol acetophenone, nitrobenzene and aniline<sup>39</sup>, or octanol, 2-octanone, 1-nitrohexane and collidine<sup>40</sup> are more suitable test solutes. In an earlier report Schwartz and Mathews<sup>41</sup> used decane, naphthalene, bipyridyl and benzil to evaluate the properties of high melting point phases. A lack of consensus as to the identity and number of test solutes to be used for phase characterization leaves this question open. To define a suitable series of test solutes to characterize stationary phase interactions a number of test solutes discussed above and some additional test solutes were evaluated. Some pertinent physical properties of the selected test solutes are summarized in Table VI<sup>42–44</sup>.

The criteria used for selection of appropriate test solutes were that retention of the solute must be dominated by one particular intermolecular interaction, retention should occur as far as possible exclusively by gas–liquid partitioning on all phases, the test solutes must have convenient retention times on all phases (neither too short nor excessively long), test solutes must elute with symmetrical peak shapes on all phases and no two test solutes should have duplicate retention characteristics on all phases. Certain test solutes representing extremes of dipolarity and/or acid–base character-

TABLE VI  
PHYSICAL AND SOLVATOCHROMIC PROPERTIES OF POTENTIAL TEST SOLUTES FOR STATIONARY PHASE CHARACTERIZATION

Test solute	Atmospheric boiling point (°C)	Dipole moment (Debyes)	Taft constants <sup>a</sup>		
			$\pi^*$	$\alpha$	$\beta$
Benzene	80	0.03-0.1	0.59	0.00	0.10
<i>n</i> -Butylbenzene	183	0.37			
1-Dodecyne	215	0			
1-Butanol	100	1.78	0.47	0.79	0.88
1-Octanol	196	1.72			
Phenol	182	1.50			
2,4,6-Trimethylphenol	220	1.40			
2-Pentanone	101	2.77			
2-Octanone	173	2.46			
Pyridine	115	2.25	0.87	0.00	0.64
2,4,6-Trimethylpyridine	172	2.26			0.78
Aniline	184	1.53			
<i>N</i> -Methylaniline	196	1.68			
<i>N,N</i> -Dimethylaniline	194	1.59	0.90	0.00	
2,6-Dimethylaniline	224	1.63			
Anisole	154	1.25	0.73	0.00	0.22
Dihexyl ether	229	1.18			
Benzodioxan	245	1.43			
Nitropropane	132	3.06			
Nitropentane	180	3.52			
Nitrobenzene	211	3.97	1.01	0.00	0.39
Benzonitrile	188	4.08	0.90	0.00	0.41
1,1,2,2-Tetrachloroethane	147	1.67	0.95		0.00
Dioxane	102	0.40	0.55	0.00	0.55
Dimethyl sulfoxide	189	3.90	1.00	0.00	0.76
Hexamethylphosphoramide	250		0.87	0.00	1.05

<sup>a</sup> Ref. 44.

istics such as dimethyl sulfoxide, hexamethylphosphoramide, tributylphosphine oxide, tripropylamine, 1-octanethiol, dicyclohexylamine, 2-ethylhexanoic acid are unsuitable test solutes due to problems with interfacial adsorption and formation of asymmetric peaks on several phases. In some cases complete adsorption by even the most exhaustively silanized columns occurred in the infinitely dilute solution region.

The test solutes benzene, *n*-butylbenzene, decane and dodecane were evaluated to provide a measure of dispersive interactions. Benzene was known to have insufficient retention for general use but was included as a bench mark for comparison. Fig. 3 shows the changes in  $(\Delta G_m^0 X)^P$  for the 24 phases evaluated using the polarity ranking of the phases to assign the arbitrary order used for the *x*-axis of the plot. All four test solutes show the same general characteristics with the exception of a small difference in behavior between the aromatic and alkane solutes on QF-1. The aromatic solutes are retained essentially by partitioning on all phases while dodecane and to a lesser extent dodecyne are retained by a mixed retention mechanism, particularly on the most polar phase. *n*-Butylbenzene has favorable retention characteristics on all phases, Table VII, and was retained as the test solute for dispersive interactions.



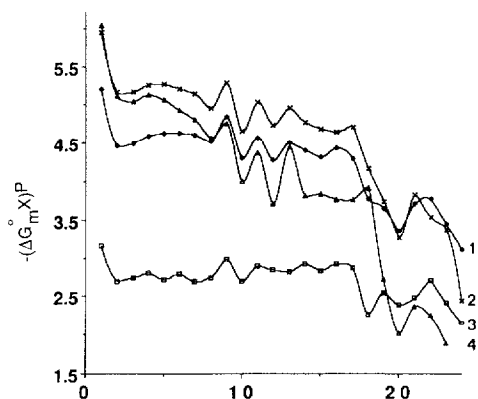


Fig. 3. Plot of  $(\Delta G_m^0 X)^P$  for  $X$  = butylbenzene (1), dodecyne (2), benzene (3) and dodecane (4). Phases are ordered by increasing polarity on the SSP scale (Table IV).

TABLE VII

CAPACITY FACTOR VALUES FOR RECOMMENDED TEST SOLUTES AT 121.4°C ON COLUMNS CONTAINING 10–15% (w/w) OF STATIONARY PHASE

Stationary phase	Recommended test solutes			
	Butylbenzene	Octanol	Benzodioxan	Nitrobenzene
Squalane	27.4	20.1	39.9	22.5
SE-30	9.7	9.8	16.2	10.4
OV-105	10.3	12.0	20.5	14.6
OV-3	12.0	12.7	25.0	16.3
OV-7	12.6	13.1	31.4	20.1
OV-11	11.3	11.3	33.6	21.1
OV-17	10.4	10.5	35.2	21.6
OV-22	9.2	9.0	36.7	21.7
PPE-5	18.4	20.8	87.2	56.4
OV-225	7.9	14.4	42.0	36.8
OV-330	14.0	31.0	82.4	56.9
QBA MES	9.6	145.2	109.0	114.2
OV-25	8.9	8.4	27.8	21.4
Carbowax 20M	7.5	21.7	74.6	52.8
TBA pTS	8.5	63.3	76.4	74.9
QBA PIC	10.6	29.9	80.2	83.9
QBA pTS	8.6	112.4	98.0	101.7
QF-1	4.4	5.8	12.4	17.4
QBA ACES	3.4	48.9	58.7	60.6
QBA TAPSO	2.4	20.5	36.8	37.5
DEGS	3.6	10.5	54.3	37.7
TCEP	4.6	13.9	75.9	62.4
QEA pTS	3.1	29.8	61.4	55.3
OV-275	2.1	5.7	30.5	29.4

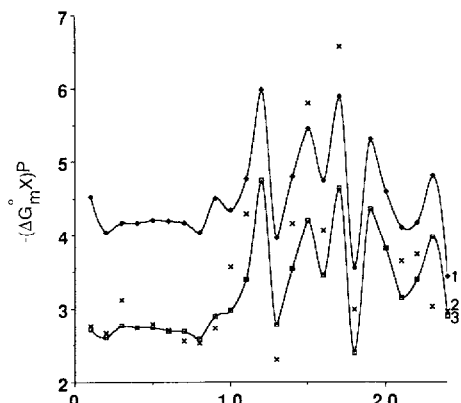


Fig. 4. Plot of  $(\Delta G_m^0 X)^P$  for X = octanol (1), 1H,1H,7H-decafluoroheptanol (2) and butanol (3) using the same order of phases given in Fig. 3. 1H,1H,7H-Decafluoroheptanol values are unavailable for some phases so the points are not connected.

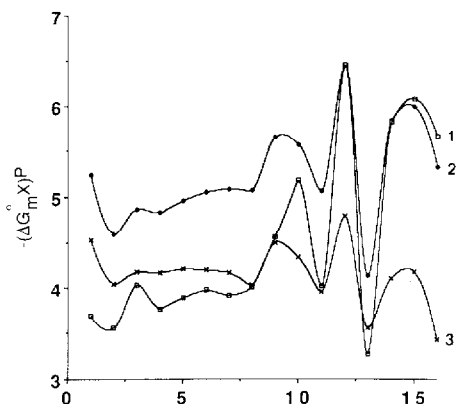


Fig. 5. Plot of  $(\Delta G_m^0 X)^P$  for X = phenol (1), 2,4,6-trimethylphenol (2) and octanol (3) using the same order of phases given in Fig. 3, skipping OV-330, QBA MES, TBA pTS, QBA pTS, QBA ACES, QBA PIC, QBA TAPSO and QEA pTS.

Alcohols and phenols were selected as test solutes for solvent proton acceptor capacity. The alcohols show both proton donor and acceptor properties with some weak orientation capacity, but in most cases their retention is dominated by solute proton donor interactions. Phenols and 1H,1H,7H-decafluoroheptanol were chosen as additional test solutes to see if more acidic test solutes would show results equivalent to those of the alcohols. They do in the general sense, Figs. 4 and 5, except that poor peak shapes or excessive retention prevented reliable data from being obtained for some phases. This makes them less useful than the alcohols as general test solutes. Octanol is largely retained by gas-liquid partitioning on all phases and has convenient

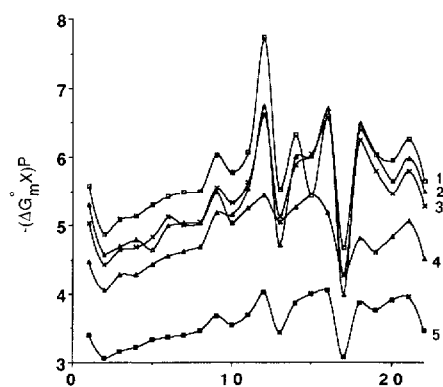


Fig. 6. Plot of  $(\Delta G_m^0 X)^P$  for X = 2,6-dimethylaniline (1), aniline (2), N-methylaniline (3), N,N-dimethylaniline (4) and pyridine (5) using the same order of phases given in Fig. 3, skipping TBA pTS and QEA pTS.

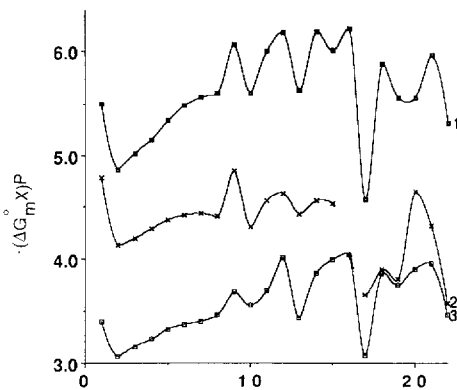


Fig. 7. Plot of  $(\Delta G_m^0 X)^P$  for X = benzodioxan (1), 2,4,6-trimethylpyridine (2) and pyridine (3) using the same order of phases given in Fig. 3, skipping TBA pTS and QEA pTS.

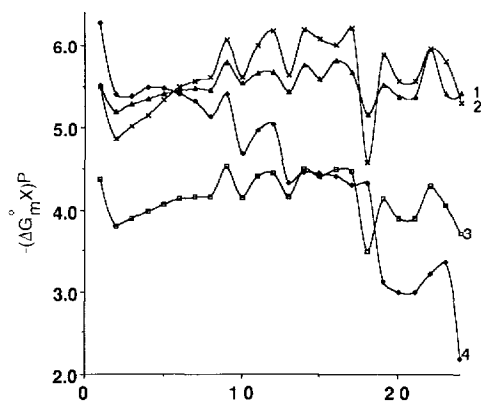


Fig. 8. Plot of  $(\Delta G_m^0 X)^P$  for X = dioxane (1), benzodioxane (2), anisole (3) and dihexyl ether (4) using the same order of phases given in Fig. 3.

retention characteristics, Table VII. Octanol was selected as the test solute for solvent proton acceptor capacity.

A number of amines, Figs. 6 and 7, and ethers, Fig. 8, were evaluated as test solutes to characterize solvent proton donor capacity. Ketones and aldehydes were also considered but these solutes behave as if they are retained by a mixed interaction mechanism. Dihexyl ether shows properties more characteristic of dodecane than the other test solutes and is not a suitable probe for solvent proton donor capacity. Aniline and N-methylaniline show substantial proton donor properties and are again unsuitable. Pyridine, 2,4,6-trimethylpyridine and N,N-dimethylaniline show consistent properties but are not eluted with acceptable peak shape from all phases. Benzodioxan, dioxane, anisole and pyridine (on those phases where a comparison is possible) show similar characteristics with benzodioxane having the most favorable retention properties. These test solutes are retained almost exclusively by gas-liquid partitioning on all phases. Benzodioxan was selected as the test solute for solvent proton donor capacity. Its choice is prejudicial on the phases tested showing significant proton donor properties. It cannot be certain that this is the case as there are few common phases in use that are thermally stable and contain a significant percentage of proton donor groups<sup>7</sup>. For the liquid organic salts QBA TAPSO, QBA ACES and TBA pTS, selected because they contain hydroxyl, amide or amine protons in their structure, it was shown that the proton donor capability of these phases is diminished compared to expectations by the involvement of these protons in the formation of intermolecular ion aggregates<sup>45</sup>. Thus, one might conclude that none of the phases tested show significant proton donor properties and the selection of a test solute for this interaction should be subject to further review. From a chemical point of view the solutes tested would seem to be reasonable.

Several nitro-containing compounds, benzonitrile and 1,1,2,2-tetrachloroethane were evaluated as test solutes to determine orientation properties, Fig. 9. 1,1,2,2-Tetrachloroethane was found to be unsuitable as it was not eluted from some phases and showed mixed orientation and proton donor characteristics. The nitro-containing compounds and benzonitrile behave in a similar manner indicating that the nitro-containing solutes were not retained by any specific mechanism peculiar to nitro

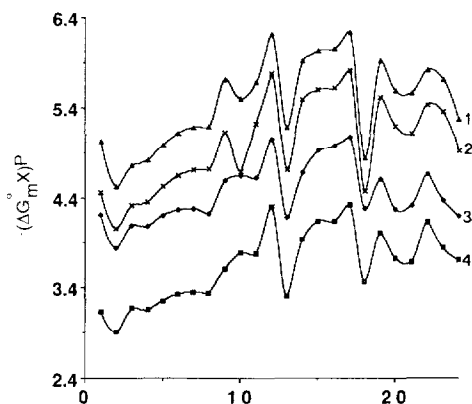


Fig. 9. Plot of  $(\Delta G_m^0 X)^P$  for X = nitrobenzene (1), benzonitrile (2), nitropentane (3) and nitropropane (4) using the same order of phases given in Fig. 3.

compounds. All solutes were retained almost exclusively by gas-liquid partitioning in the general order 1-nitropentane < benzonitrile < nitrobenzene. Nitrobenzene was arbitrarily selected as the test solute for orientation interactions as either 1-nitropropane or benzonitrile would have been equally acceptable. In terms of retention characteristics 1-nitrohexane might be preferable to 1-nitropropane.

TABLE VIII

SELECTIVITY RANKING OF STATIONARY PHASES BY THEIR ABILITY TO INTERACT WITH *n*-BUTYLBENZENE

Stationary phase	$(\Delta G_m^0 X)^P$	$\delta(\Delta G_m^0 X)_{SQ}^P$
OV-275	$-3.105 \pm 0.097$	$2.085 \pm 0.100$
QBA TAPSO	$-3.356 \pm 0.066$	$1.834 \pm 0.070$
QEA pTS	$-3.449 \pm 0.034$	$1.740 \pm 0.043$
QBA ACES	$-3.650 \pm 0.033$	$1.540 \pm 0.042$
DEGS	$-3.706 \pm 0.051$	$1.483 \pm 0.057$
TCEP	$-3.764 \pm 0.027$	$1.426 \pm 0.037$
QF-1	$-3.768 \pm 0.029$	$1.422 \pm 0.039$
QBA MES	$-4.265 \pm 0.048$	$0.925 \pm 0.055$
QBA pTS	$-4.293 \pm 0.028$	$0.897 \pm 0.038$
OV-225	$-4.300 \pm 0.044$	$0.890 \pm 0.051$
TBA pTS	$-4.302 \pm 0.026$	$0.887 \pm 0.037$
Carbowax 20M	$-4.394 \pm 0.009$	$0.794 \pm 0.027$
QBA PIC	$-4.424 \pm 0.012$	$0.765 \pm 0.029$
SE-30	$-4.460 \pm 0.081$	$0.730 \pm 0.085$
OV-105	$-4.486 \pm 0.046$	$0.704 \pm 0.051$
OV-25	$-4.495 \pm 0.013$	$0.695 \pm 0.029$
OV-22	$-4.515 \pm 0.022$	$0.674 \pm 0.034$
OV-330	$-4.564 \pm 0.013$	$0.626 \pm 0.029$
OV-3	$-4.579 \pm 0.026$	$0.611 \pm 0.037$
OV-17	$-4.597 \pm 0.030$	$0.593 \pm 0.040$
OV-11	$-4.619 \pm 0.048$	$0.570 \pm 0.054$
OV-7	$-4.620 \pm 0.044$	$0.570 \pm 0.051$
PPE-5	$-4.838 \pm 0.024$	$0.361 \pm 0.036$
Squalane	$-5.199 \pm 0.026$	0

Stationary phase selectivity in order of increasing strength as determined by  $(\Delta G_m^0 X)^P$  or  $\delta(\Delta G_m^0 X)_{SQ}^P$  is summarized in Table VIII for *n*-butylbenzene, Table IX for nitrobenzene, Table X for 1-octanol and Table XI for benzodioxan. As would be anticipated retention of *n*-butylbenzene on squalane exceeds that on all other phases. The weakest interactions are shown by DEGS, QF-1, OV-275 and some of the liquid organic salts. The unusual behavior of QF-1 is explained by the low affinity of fluorinated compounds for hydrocarbons as discussed in detail elsewhere<sup>33,34</sup>. There is a poor correlation between SSP and  $(\Delta G_m^0 X)^P$  and  $\delta(\Delta G_m^0 X)_{SQ}^P$  where X = *n*-butylbenzene, particularly for the first five phases of minimum polarity (squalane, SE-30, OV-105, OV-3 and OV-7) which are displaced to larger values of SSP compared to the other phases. The correlation coefficient if the five phases of minimum polarity are excluded is  $r = 0.94$ . The two scales are therefore not redundant as SSP will reflect solvent interactions characteristic of *n*-alkanes and  $(\Delta G_m^0 X)^P$  characteristic of aromatic hydrocarbons. These differences probably arise from the difference in polarizability and the availability of some weak electron donor capacity for aromatic compounds. Considering the uncertainty in the data for benzene (due to its low retention) there is a reasonable correlation between  $(\Delta G_m^0 X)^P$  for benzene and *n*-butylbenzene using all phases,  $r = 0.88$ , and supports the view that the inclusion of benzene into the McReynolds test set was to allow a better estimate of retention indices by accommodating the specific properties of aromatic compounds.

TABLE IX

SELECTIVITY RANKING OF STATIONARY PHASES BY THEIR ABILITY TO INTERACT WITH NITROBENZENE

Stationary phase	$(\Delta G_m^0 X)^P$	$\delta(\Delta G_m^0 X)_{SQ}^P$
SE-30	$-4.519 \pm 0.069$	$0.505 \pm 0.074$
OV-105	$-4.755 \pm 0.046$	$0.269 \pm 0.053$
OV-3	$-4.812 \pm 0.038$	$0.218 \pm 0.046$
QF-1	$-4.833 \pm 0.023$	$0.190 \pm 0.034$
OV-7	$-4.984 \pm 0.045$	$0.039 \pm 0.052$
Squalane	$-5.023 \pm 0.026$	0
OV-11	$-5.114 \pm 0.045$	$-0.091 \pm 0.052$
OV-25	$-5.172 \pm 0.025$	$-0.149 \pm 0.036$
OV-17	$-5.179 \pm 0.029$	$-0.156 \pm 0.039$
OV-22	$-5.181 \pm 0.022$	$-0.158 \pm 0.034$
OV-275	$-5.254 \pm 0.041$	$-0.231 \pm 0.048$
OV-225	$-5.494 \pm 0.016$	$-0.471 \pm 0.030$
DEGS	$-5.549 \pm 0.059$	$-0.526 \pm 0.064$
QBA TAPSO	$-5.573 \pm 0.002$	$-0.554 \pm 0.026$
OV-330	$-5.672 \pm 0.008$	$-0.649 \pm 0.027$
QEA pTS	$-5.701 \pm 0.022$	$-0.678 \pm 0.033$
PPE-5	$-5.711 \pm 0.026$	$-0.688 \pm 0.037$
TCEP	$-5.806 \pm 0.006$	$-0.783 \pm 0.026$
QBA ACES	$-5.907 \pm 0.009$	$-0.884 \pm 0.027$
Carbowax 20M	$-5.912 \pm 0.033$	$-0.888 \pm 0.042$
TBA pTS	$-6.027 \pm 0.024$	$-1.004 \pm 0.035$
QBA PIC	$-6.046 \pm 0.016$	$-1.023 \pm 0.030$
QBA MES	$-6.206 \pm 0.052$	$-1.183 \pm 0.058$
QBA pTS	$-6.232 \pm 0.028$	$-1.209 \pm 0.038$

TABLE X

SELECTIVITY OF STATIONARY PHASES BY THEIR ABILITY TO INTERACT WITH 1-OCTANOL

Stationary phase	$(\Delta G_m^0 X)^P$	$\delta(\Delta G_m^0 X)_{SQ}^P$
OV-275	$-3.865 \pm 0.077$	$1.096 \pm 0.082$
QF-1	$-3.987 \pm 0.026$	$0.974 \pm 0.037$
OV-25	$-4.381 \pm 0.000$	$0.5794 \pm 0.027$
OV-22	$-4.469 \pm 0.060$	$0.492 \pm 0.065$
SE-30	$-4.477 \pm 0.053$	$0.484 \pm 0.060$
DEGS	$-4.540 \pm 0.044$	$0.421 \pm 0.052$
OV-17	$-4.602 \pm 0.031$	$0.359 \pm 0.041$
OV-3	$-4.605 \pm 0.050$	$0.356 \pm 0.057$
OV-105	$-4.607 \pm 0.042$	$0.354 \pm 0.049$
TCEP	$-4.609 \pm 0.010$	$0.352 \pm 0.029$
OV-11	$-4.629 \pm 0.038$	$0.332 \pm 0.046$
OV-7	$-4.641 \pm 0.055$	$0.320 \pm 0.061$
OV-225	$-4.769 \pm 0.034$	$0.192 \pm 0.043$
PPE-5	$-4.931 \pm 0.028$	$0.029 \pm 0.039$
Squalane	$-4.961 \pm 0.027$	0
QBA TAPSO	$-5.0181 \pm 0.005$	$-0.057 \pm 0.027$
QBA PIC	$-5.174 \pm 0.021$	$-0.214 \pm 0.034$
OV-330	$-5.196 \pm 0.031$	$-0.235 \pm 0.041$
Carbowax 20M	$-5.221 \pm 0.015$	$-0.260 \pm 0.031$
QEA pTS	$-5.233 \pm 0.023$	$-0.272 \pm 0.035$
QBA ACES	$-5.735 \pm 0.046$	$-0.775 \pm 0.053$
TBA pTS	$-5.883 \pm 0.006$	$-0.923 \pm 0.027$
QBA pTS	$-6.314 \pm 0.028$	$-1.353 \pm 0.039$
QBA MES	$-6.366 \pm 0.130$	$-1.405 \pm 0.133$

The strongest orientation interactions are shown by the liquid organic salts with Carbowax 20M, TCEP, OV-330 and DEGS being the most dipolar of the non-ionic phases. The poly(dicyanoallylsiloxane), OV-275, shows only intermediate dipolarity and its status as a polar phase seems to depend largely on its unusually low affinity for alkane and aromatic groups. The least dipolar interactions are shown by the polysiloxane phases lacking a cyanoalkyl group and squalane in keeping with expectations. There is a good correlation between  $(\Delta G_m^0 X)^P$  for 1-nitropropane and nitrobenzene,  $r = 0.95$ . The improvement in the correlation coefficient compared to the data for benzene and *n*-butylbenzene is probably due in large part to the smaller uncertainties in the data for 1-nitropropane.

The strongest proton acceptor interactions are shown by the liquid organic salts as would be anticipated from their published chromatographic applications<sup>45,46</sup>. Carbowax 20M and OV-330 show the strongest proton acceptor interactions of the non-ionic phases. At first sight the position of squalane in Table X might look anomalous and we will return to this point presently. There are a large number of phases just below squalane with similar values for  $(\Delta G_m^0 X)^P$  indicating a narrow range of selectivity for a large number of the phases in Table X. Among these phases are OV-275, DEGS, TCEP which show selective orientation and/or weak dispersive-type interactions. Again, given the uncertainties in the data for the McReynolds probe *n*-butanol there is a good correlation with octanol,  $r = 0.91$ , for the  $(\Delta G_m^0 X)^P$  values.

TABLE XI

SELECTIVITY RANKING OF STATIONARY PHASES BY THEIR ABILITY TO INTERACT WITH BENZODIOXAN

Stationary phase	$(\Delta G_m^0 X)^P$	$\delta(\Delta G_m^0 X)_{SQ}^P$
QF-1	$-4.571 \pm 0.017$	$0.923 \pm 0.033$
SE-30	$-4.866 \pm 0.083$	$0.629 \pm 0.087$
OV-105	$-5.010 \pm 0.070$	$0.485 \pm 0.076$
OV-3	$-5.149 \pm 0.033$	$0.345 \pm 0.044$
OV-275	$-5.302 \pm 0.044$	$0.192 \pm 0.052$
OV-7	$-5.330 \pm 0.044$	$0.164 \pm 0.053$
OV-11	$-5.481 \pm 0.041$	$0.013 \pm 0.050$
Squalane	$-5.494 \pm 0.029$	0
QBA TAPSO	$-5.556 \pm 0.0170$	$-0.061 \pm 0.033$
OV-17	$-5.560 \pm 0.033$	$-0.065 \pm 0.044$
OV-22	$-5.560 \pm 0.023$	$-0.103 \pm 0.037$
OV-225	$-5.601 \pm 0.103$	$-0.1078 \pm 0.107$
OV-25	$-5.628 \pm 0.022$	$-0.133 \pm 0.036$
QEA pTS	$-5.787 \pm 0.017$	$-0.292 \pm 0.033$
DEGS	$-5.835 \pm 0.058$	$-0.340 \pm 0.064$
QBA ACES	$-5.876 \pm 0.018$	$-0.377 \pm 0.033$
TCEP	$-5.954 \pm 0.009$	$-0.460 \pm 0.030$
OV-330	$-5.968 \pm 0.004$	$-0.473 \pm 0.090$
QBA PIC	$-6.006 \pm 0.012$	$-0.518 \pm 0.031$
TBA pTS	$-6.040 \pm 0.027$	$-0.546 \pm 0.039$
PPE-5	$-6.059 \pm 0.032$	$-0.565 \pm 0.042$
QBA MES	$-6.169 \pm 0.051$	$-0.674 \pm 0.058$
Carbowax 20M	$-6.182 \pm 0.022$	$-0.6877 \pm 0.036$
QBA pTS	$-6.202 \pm 0.024$	$-0.708 \pm 0.037$

The ranking of phases by their proton donor capacity is rather more compressed than the other scales. The most selective phases are the liquid organic salts, Carbowax 20M, PPE-5 and OV-330. These are also the phases with the highest dipolarity or contain ether linkages. Since none of the most selective phases contain obvious proton donor groups we suspect that the ranking order indicates increasing general solubility of benzodioxan in the stationary phases rather than specific proton donor interactions. TBA pTS, QBA ACES and QBA TAPSO were originally incorporated into this study as examples of proton donor solvents, but as mentioned earlier, the protons available in these solvents are likely involved in anion aggregation making them less available to the solute<sup>16,45</sup>. The need for thermally stable strong proton donor solvents in gas chromatography is probably unfulfilled<sup>7,47</sup>.

The Rohrschneider/McReynolds schemes of solvent selectivity incorporated squalane into the protocol as a non-polar reference phase. To determine selectivity a reference phase is in fact unnecessary as it functions only to scale the data and does not affect the magnitude of difference between phases<sup>48</sup>. On theoretical grounds a non-polar reference phase is a reasonable choice as the only solute-solvent interactions involved are dispersion and induction. From a thermodynamic point of view a suitable reference phase would be a chemically defined substance exhibiting minimum selectivity and of sufficiently high molecular weight so as to minimize variations in free energies due to molecular weight differences as discussed by Fritz and Kovats<sup>31</sup>. We have preferred to use the  $(\Delta G_m^0 X)^P$  scale in this paper rather than

$\delta(\Delta G_m^0 X)_{SQ}^P$  for practical reasons. Of the phases tested squalane is the only one of significant vapor pressure and poor film stability at the measurement temperature. In terms of selectivity it is the sixth least selective for nitrobenzene, the tenth least selective for 1-octanol and the eight least selective for benzodioxan. It does not meet the thermodynamic criteria for use as a non-selective reference phase. The question is whether this is due to experimental or chemical reasons. The increased retention of 1-octanol and nitrobenzene compared to the other phases of low selectivity might be interpreted as indicating that the silanization procedure used for support deactivation was inadequate. On the other hand, horizontal plots of  $V_N^*/V_L$  vs.  $1/V_L$  were obtained and the uncertainty in the values for the gas-liquid partition coefficients are similar to other phases (reflecting mainly the inaccuracy of determining the phase loading). Note that the gas-liquid partition coefficients are obtained from four independent columns of different phase loading and not just from a single column, packing or experiment. The consistency in the gas-liquid partition coefficients from column to column would only be possible if the contribution from adsorption was the same for all columns and increased in proportion to the phase loading. A set of circumstances that would be very unusual. From Table IV it can be seen that the capacity of squalane for non-polar interactions with a methylene group easily exceeds that of the other phases and the unexpected retention of 1-octanol compared to other weakly selective phases could be due to a greater affinity for the alkane portion of the test solute. This question cannot be resolved at present. In further studies we will investigate the influence of support type and surface area as an additional parameter for determining gas-liquid partition coefficients for squalane and other phases of low selectivity such as Apolane-87 and Apiezon MH which are more stable at the analysis temperature.

The molal standard state was used in calculating the free energies in Tables VIII to XI to avoid complications from differences in the molecular weights of the various phases. In practice the selectivity ranking of the phases is similar if either the molal or molar standard states are used as can be seen from the data in Fig. 10 and Table XII. The two scales are related by a linear equation of the type:

$$(\Delta G_m^0 X)^P = E(\Delta G_k^0 X)^P + F \quad (11)$$

The slopes,  $E$ , vary from 0.91 to 1.07 with correlation coefficients,  $r$ , between 0.96 and 1.00. Since most of the slopes deviate from 1.00 the two scales are not identical but the

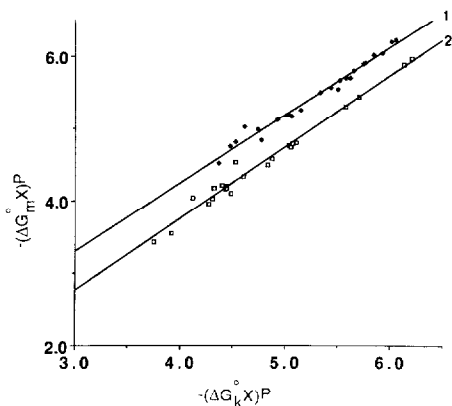


Fig. 10. Plot of  $(\Delta G_m^0 X)^P$  against  $(\Delta G_k^0 X)^P$  for X = nitrobenzene (1) and octanol (2).



TABLE XII

CORRELATION OF SELECTIVITY SCALES BASED ON  $(\Delta G_m^0 X)^P$  AND  $(\Delta G_k^0 X)^P$  FROM EQN. 11

Test solute	Linear regression coefficients			
	<i>E</i>	<i>F</i>	<i>r</i>	<i>n</i>
Butylbenzene	1.0794	0.1322	0.99	24
1-Dodecyne	1.0593	-0.0721	1.00	24
Octanol	0.9900	-0.2048	0.99	24
1H,1H,7H-Dodecafluoroheptanol	0.9832	0.1875	1.00	21
Phenol	0.9504	0.0097	1.00	16
2,4,6-Trimethylphenol	0.9659	0.0806	0.99	14
Aniline	0.9563	0.4113	1.00	22
N-Methylaniline	0.9505	0.4447	0.99	21
N,N-Dimethylaniline	0.9413	0.4592	0.95	22
2,6-Dimethylaniline	0.9330	0.5481	0.98	22
1-Nitropentane	0.9535	0.3676	0.98	22
Nitrobenzene	0.9398	0.4878	0.99	24
Benzonitrile	0.9107	0.6115	0.99	24
2,4,6-Trimethylpyridine	0.9712	0.3088	0.96	21
Anisole	0.9800	0.2492	0.98	22
Benzodioxan	0.9194	0.6273	0.99	23
Dihexyl ether	1.0465	0.0140	1.00	24
Nonanal	1.0375	0.0202	0.98	24

differences are small. In terms of ranking of the phases only those phases with similar values for the free energies would possibly be switched. Given the uncertainties in the values of  $K_L$  (Table XI) using the molal or molar standard states does not lead to serious inconsistencies in the determination of solvent selectivity.

In conclusion, two new scales of solvent strength and selectivity have been developed. These scales are based on a different theoretical background than the familiar Rohrschneider/McReynolds approach and lead to different conclusions. In fact the  $(\Delta G_m^0 X)^P$  scale can be mathematically related to the retention index differences of McReynolds by a complex expression under conditions where retention of the index standards and test solutes occurs exclusively by gas-liquid partitioning<sup>15</sup>. It is shown that any agreement between the two scales is purely coincidental as the values for the retention index differences are conditioned largely by the behavior of the index standards. The two new scales proposed here are largely in keeping with chemical intuition but will be subject to revision as further data is collected and alternative methods of data analysis becomes possible. The raw experimental data which are unbiased by the method of interpretation, we hope will be of value to others in testing solution models of relevance to gas chromatography.

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