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CONSIDERATIONS FOR USING THE SOLVENT SELECTIVITY TRIANGLE APPROACH FOR STATIONARY PHASE CHARACTERIZATION

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SUMMARY

The use of solvent selectivity parameters (X_e , X_n , X_d) for stationary phase characterization is compromised by a failure to allow for interfacial adsorption of test solutes and *n*-alkane retention index markers in the recommended calculation method and by inadequate retention of the test solutes ethanol, nitromethane, and dioxane on phases of low polarity. There is also a lack of constancy in the relative position of phases in the selectivity triangle as the identity of the test solutes is changed. The low partitioning of *n*-alkanes on polar phases such as DEGS, OV-275, TCEP, EAN and PAN precludes calculation of solvent selectivity parameters using retention index differences. The partial molar Gibbs free energy of solution for the test solutes derived from the gas-liquid partition coefficients corrected for interfacial adsorption allows the universal calculation of solvent selectivity parameters for all phases. The position of individual phases in selectivity groups is similar for selectivity parameters calculated using either corrected retention indices or Gibbs free energy differences except that all phases are displaced to the right in the triangle constructed using free energy differences resulting from weak interactions for the tested phases with the proton acceptor probe dioxane. There is good agreement between the solvent strength calculated from the energy differences, the partial molar Gibbs free energy of solution for a methylene group, and Snyder's P' values for non-polar and moderately polar phases. Polar phases show anomalous behaviour on the different scales. Recommendations for further improvements in the solvent selectivity parameter approach to stationary phase characterization are made.

INTRODUCTION

Snyder¹ introduced the solvent strength parameter (P') and solvent selectivity parameters (X_e , X_n , X_d) to characterize the fundamental properties of solvents used in gas and liquid chromatography. The test solutes ethanol, dioxane and nitromethane were selected as probes to express the contribution made by proton donor-acceptor complexation and orientation interactions to the solvent strength. By plotting the data with triangular coordinates solvents of similar selectivity are easily identified and preferred solvents for stationary phase selectivity optimization identified. In this context Klee *et al.*² classified several commonly used gas chromatographic stationary

phases and commented on the current lack of phases close to the apices of the selectivity triangle which would provide the most varied properties for selectivity optimization. Shah *et al.*³ noted that the position of a solvent within the selectivity triangle varied with the selection of the test solutes including the use of homologues of the original test solutes used by Snyder. Betts⁴ suggested that 2-octyne, *n*-butanol, and pyridine were more appropriate probes than those suggested by Snyder for estimating polar interactions. All of these studies can be seen to be related to earlier work by Brown⁵ who used the retention volumes of various test probes on different stationary phases plotted as triangular coordinates to indicate selective stationary phase interactions. For a review of the use of the solvent selectivity triangle approach to stationary phase characterization see ref. 6.

It is noteworthy that in all the above studies it is assumed that the retention of the test probes and the *n*-alkanes used to calculate retention index differences are controlled by gas-liquid partitioning for all phases. Previously⁷⁻⁹ we have shown that failure to appreciate the importance of interfacial adsorption as a retention mechanism can lead to poor stationary phase classification using the McReynolds stationary phase classification scheme. In this report the role of interfacial adsorption in the misclassification of selectivity parameters is assessed for 15 stationary phases spanning a wide range of solvent strength and an improved calculation procedure based on the partial molar Gibbs free energy of solution for the Snyder probes is recommended to eliminate errors arising from the use of the retention index scheme for stationary phase classification.

EXPERIMENTAL

The silicone polymers OV-105 (cyanopropylmethyltrimethylsilicone), OV-17 (phenylmethylsilicone), OV-330 (dimethylsilicone/Carbowax copolymer), OV-225 (cyanopropylmethylphenylmethylsilicone), and OV-275 (dicyanoallylsilicone) were obtained from Ohio Valley Specialty Chemicals (Marietta, OH, U.S.A.). Squalane, QF-1 (trifluoropropylmethylsilicone), Carbowax 20M [poly(ethylene glycol)], DEGS [poly(diethylene glycol succinate)], TCEP [1,2,3-tris(2-cyanoethoxy)propane], Chromosorb W-AW (60-80 mesh), and column conditioner (a mixture of silanizing reagents No. A7682) were obtained from Anspec (Ann Arbor, MI, U.S.A.). Ethylammonium nitrate (EAN), *n*-propylammonium nitrate (PAN), *n*-butylammonium thiocyanate (BAT), *sec.*-butylammonium thiocyanate (sBAT), and di-*n*-propylammonium thiocyanate (DPAT) were prepared as described previously^{10,11}. Other standards and reagents were general laboratory grade in the highest purity available.

Column packings containing from 5 to 20% (w/w) of liquid phase on Chromosorb W-AW were prepared using the rotary evaporator technique. The damp packings were dried in a fluidized-bed drier, sieved, and packed into glass columns (3.0 m × 2.0 mm I.D.) with the aid of vacuum suction and gentle vibration. The packings prepared with squalane, OV-105, OV-17, QF-1 and OV-225 were thoroughly silanized *in situ* by repeated injection of 50 μ l of column conditioner at 100°C followed by conditioning at the same temperature until invariant retention times and symmetrical peak shapes for the test solutes were obtained. Accurate phase loadings were determined by evaporation for squalane and the liquid organic salts^{7,12} and by Soxhlet extraction for the higher-molecular-weight polymeric phases¹³.

For column evaluation a Varian 3700 gas chromatograph with a heated on-column injector and flame-ionization detector was used. The nitrogen carrier gas flow-rate was accurately measured with a thermostatted soap-film bubble meter and set to approximately 20 ml/min. All measurements were made isothermally at $80.8 \pm 0.2^\circ\text{C}$. Samples were injected as headspace vapors with a gas-tight syringe to approximate the conditions for infinite dilution. Sample sizes were varied to insure that all data were measured in the Henry's law region and retention times independent of sample size were obtained. All peaks were symmetrical.

The net retention volume per gram of packing corrected to zero column pressure drop for the test solutes and *n*-alkanes were calculated according to eqn. 1.

$$\ln V_N^* = \ln \left[\frac{3}{2} (t_R - t_M) \frac{F_0}{W} \left(\frac{T_c}{T_a} \right) \left(1 - \frac{P_w}{P_a} \right) \left(\frac{P^2 - 1}{P^3 - 1} \right) \right] - \frac{3\beta}{4} P_a \left(\frac{P^4 - 1}{P^3 - 1} \right) \quad (1)$$

- where V_N^* = net retention volume per gram of packing corrected to zero column pressure drop
 t_R = solute retention time
 t_M = column dead time (assumed equal to the retention time of methane at T_c)
 F_0 = carrier gas flow-rate at the column outlet
 W = weight of column packing
 T_c = column temperature (K)
 T_a = ambient temperature (K)
 P_w = saturated water vapor pressure at T_a
 P_a = ambient pressure (mmHg)
 P = column pressure drop (P_i/P_a)
 P_i = column inlet pressure (mmHg)
 β = $(2B_{12} - V_1^0)/RT_c$
 B_{12} = second interaction virial coefficient (solute-carrier gas)
 V_1^0 = solute molar volume
 R = universal gas constant

A mercury manometer was used to determine the column pressure drop (± 1 mmHg). The second interaction virial coefficients were taken from the compilations of Dymond and Smith¹⁴ and Driesbach¹⁵, or if unavailable calculated by the method of corresponding states¹⁶.

Gas-liquid partition coefficients were estimated by linear extrapolation of plots of V_N^*/V_L vs. $1/V_L$ based on eqn. 2^{7,17,18}

$$\frac{V_N^*}{V_L} = K_L + B \cdot \frac{1}{V_L} \quad (2)$$

- where V_L = volume of liquid phase per gram of packing
 K_L = gas-liquid partition coefficient
 B = coefficient accounting for interfacial adsorption

Values for the adjusted retention time and gas-liquid partition coefficients for

TABLE I
RETENTION DATA FOR TEST SOLUTES

Stationary phase	Adjusted retention time (min)*			Gas-liquid partition coefficient \pm standard deviation		
	Ethanol	Nitromethane	Dioxane	Ethanol	Nitromethane	Dioxane
Squalane	0.17	0.33	1.72	7.2 \pm 0.2	15.9 \pm 0.7	81.4 \pm 0.7
OV-17	0.15	0.65	1.48	13.5 \pm 0.7	57.5 \pm 1.6	129.2 \pm 3.2
OV-105	0.32	0.56	1.29	18.4 \pm 2.7	34.9 \pm 0.9	84.7 \pm 2.3
OV-330	0.52	1.87	1.90	43.9 \pm 2.1	160.0 \pm 6.4	161.0 \pm 5.7
OV-225	0.46	2.03	2.13	32.8 \pm 1.3	143.3 \pm 8.7	148.1 \pm 9.6
QF-1	0.13	0.84	0.95	14.5 \pm 1.1	91.0 \pm 2.4	101.6 \pm 1.7
Carbowax 20M	1.24	5.41	3.14	76.1 \pm 0.6	341.7 \pm 2.7	199.6 \pm 0.7
DPAT	2.31	3.05	3.07	174.0 \pm 5.3	242.0 \pm 3.3	229.8 \pm 6.0
DEGS	0.69	2.25	1.95	84.4 \pm 2.0	273.3 \pm 6.1	236.1 \pm 4.5
BAT	2.75	2.08	4.73	237.5 \pm 5.5	178.2 \pm 3.0	406.3 \pm 9.6
sBAT	3.97	2.76	6.80	293.5 \pm 7.3	205.9 \pm 6.5	505.2 \pm 11.7
TCEP	0.74	3.95	2.60	72.2 \pm 0.9	375.4 \pm 5.7	245.9 \pm 3.3
OV-275	0.46	2.25	1.26	41.1 \pm 2.6	232.4 \pm 6.8	126.4 \pm 4.7
PAN	3.79	3.81	4.39	167.7 \pm 1.5	168.4 \pm 0.9	196.4 \pm 1.7
EAN	4.52	5.10	5.20	177.2 \pm 1.0	203.3 \pm 1.3	207.5 \pm 2.5

* 3.0 m \times 2 mm I.D. column with 12–15% (w/w) of phase on Chromosorb W-AW (60–80 mesh).

ethanol, nitromethane, and dioxane on all phases are given in Table I. The partition coefficients for the *n*-alkane and 2-alkanone retention index markers were fitted to eqn. 3. The coefficients obtained by linear regression are summarized in Table II.

TABLE II
COEFFICIENTS FOR CALCULATING PARTITION COEFFICIENTS FOR *n*-ALKANES AND 2-ALKANONES (EQN. 3)

Stationary phase	<i>n</i> -Alkanes			2-Alkanones		
	<i>A</i>	<i>D</i>	Correlation coefficient (r^2)	<i>A</i>	<i>D</i>	Correlation coefficient (r^2)
Squalane	0.361	-0.3746	1.000	0.358	0.7673	1.000
OV-17	0.325	-0.5596	0.999	0.317	1.0517	0.999
OV-105	0.314	-0.3339	1.000	0.311	0.9841	0.999
OV-330	0.302	-0.6023	1.000	0.298	1.1844	0.999
OV-225	0.293	-0.6556	1.000	0.284	1.2894	0.999
QF-1	0.262	-0.3152	1.000	0.270	1.3499	0.999
Carbowax 20M	0.264	-0.5754	0.999	0.265	1.2939	0.999
DPAT	0.228	-0.6058	1.000	0.239	1.5658	0.999
DEGS	—	—	—	0.218	1.3653	0.999
BAT	0.223	-0.8211	0.999	0.215	1.6994	0.997
sBAT	0.188	-0.5733	0.998	0.204	1.8350	0.998
TCEP	—	—	—	0.199	1.5552	0.999
OV-275	—	—	—	0.180	1.3233	0.998
PAN	—	—	—	0.166	1.4033	0.997
EAN	—	—	—	0.088	1.5565	0.991

$$\log K_L = A(n) + D \quad (3)$$

where A and D = experimentally derived constants

n = number of carbon atoms for the n -alkanes or the number of carbon atoms minus 2 for the 2-alkanones.

The retention index for each test solute was determined from the adjusted retention time using the standard procedure¹⁹. Retention index values corrected for interfacial adsorption were calculated using eqn. 4⁷

$$I_{PH}^c(P) = 100z + 100 \left[\frac{\log K_L^P - \log K_L^z}{\log K_L^{z+1} - \log K_L^z} \right] \quad (4)$$

where $I_{PH}^c(P)$ = retention index for probe P corrected for interfacial adsorption on phase PH

K_L^P = gas-liquid partition coefficient for probe P

K_L^z = gas-liquid partition coefficient for a n -alkane with z carbon atoms eluting immediately before probe P

K_L^{z+1} = gas-liquid partition coefficient for an n -alkane with $z+1$ carbon atoms eluting after probe P.

Retention index values of ethanol, nitromethane and dioxane on all phases are summarized in Table III.

The solvent polarity parameter (P') and solvent selectivity parameters (X_e , X_n and X_d) were calculated according to the method of Snyder¹. The solvent polarity parameter is obtained from eqn. 5

TABLE III
RETENTION INDEX VALUES FOR THE TEST SOLUTES

Stationary phase	Retention index values					
	Uncorrected			Corrected		
	Ethanol	Nitromethane	Dioxane	Ethanol	Nitromethane	Dioxane
Squalane	369	449	643	353	451	643
OV-17	519	715	824	492	714	825
OV-105	533	608	722	555	668	772
OV-330	749	933	935	755	940	940
OV-225	740	963	970	736	968	976
QF-1	564	874	895	556	878	896
Carbowax 20M	919	1150	1065	934	1178	1093
DPAT	1225	1276	1277	1255	1312	1308
DEGS	1107	1292	1270			
BAT	1395	1342	1501	1426	1374	1538
sBAT	1498	1428	1599	1635	1554	1767
TCEP	1182	1477	1406			
OV-275	1131	1385	1294			
PAN	1437	1438	1460			
EAN	1612	1640	1645			

$$P' = 1.2 + \Sigma \Delta I_i^c \cdot \frac{A}{100} \quad (5)$$

where P' = solvent polarity parameter
 $\Sigma \Delta I_i^c$ = $\Delta I_e^c + \Delta I_n^c + \Delta I_d^c$
 ΔI_i^c = $I_{PH}^c(i) - I_{SQ}^c(i)$
 $I_{PH}^c(i)$ = corrected retention index for probe i on phase PH
 $I_{SQ}^c(i)$ = corrected retention index for probe i on squalane
 A = slope of the plot of $\log K_L$ vs. carbon number for the n -alkanes (Table II)

The subscripts e, n and d refer to ethanol, nitromethane and dioxane, respectively. The solvent selectivity parameters (X_e, X_n, X_d) are defined in turn by eqn. 6. Values for the solvent polarity parameter and solvent selectivity parameters are summarized in Table IV.

$$X_i = \frac{\Delta I_i^c}{\Sigma \Delta I_i^c} = \frac{\Delta I_i^c}{\Delta I_e^c + \Delta I_n^c + \Delta I_d^c} \quad (6)$$

The partial molar Gibbs free energy of solution for a methylene group was calculated using eqn. 7 and the coefficients summarized in Table II²⁰

$$\Delta G_k^0(\text{CH}_2) = -2.3 RT_c A \quad (7)$$

TABLE IV

SOLVENT POLARITY AND SOLVENT SELECTIVITY PARAMETERS

Stationary phase	Gibbs free energy per methylene group (cal/mol)		Solvent polarity parameter (P')*	Solvent selectivity parameters		
	<i>n</i> -Alkanes	2-Alkanones		X_e	X_n	X_d
Squalane	-585	-579	1.20			
OV-17	-525	-513	3.10	0.24	0.45	0.31
OV-105	-508	-503	2.76	0.40	0.44	0.16
OV-330	-488	-482	4.79	0.34	0.41	0.25
OV-225	-469	-459	4.78	0.31	0.42	0.27
QF-1	-424	-437	3.51	0.24	0.48	0.28
Carbowax 20M	-427	-428	5.84	0.33	0.41	0.26
DPAT	-369	-386	6.74	0.37	0.35	0.27
DEGS		-352	(7.28)			
BAT	-361	-347	7.65	0.37	0.32	0.31
TCEP		-322	(8.03)			
sBAT	-304	-330	7.80	0.37	0.31	0.32
OV-275		-291	(8.81)			
PAN		-268	(9.41)			
EAN		-142	(12.58)			

* Values in parentheses were estimated from eqn. 13.

TABLE V
PARTIAL MOLAR AND MOLAL GIBBS FREE ENERGY OF SOLUTION FOR THE TEST SOLUTES

Stationary phase	Partial molar Gibbs free energy (kcal/mol)			Partial molal Gibbs free energy (kcal/mol)		
	Ethanol	Nitromethane	Dioxane	Ethanol	Nitromethane	Dioxane
Squalane	-1.3919	-1.9517	-3.1037	-1.8204	-2.3801	-3.5321
OV-17	-1.8284	-2.8493	-3.4280	-2.0391	-3.0599	-3.6386
OV-105	-2.0481	-2.5033	-3.1314	-2.3486	-2.8037	-3.4319
OV-330	-2.6588	-3.5669	-3.5823	-2.8582	-3.7663	-3.7817
OV-225	-2.4536	-3.4910	-3.5238	-2.6676	-3.7051	-3.7379
QF-I	-1.8812	-3.1719	-3.2651	-1.9945	-3.2852	-3.3783
Carbowax 20M	-3.0463	-4.1020	-3.7344	-3.2450	-4.3007	-3.9331
DPAT	-3.6273	-3.8593	-3.8324	-3.9227	-4.1547	-4.1278
DEGS	-3.1186	-3.9448	-3.8508	-3.2263	-4.0526	-3.9585
BAT	-3.8463	-3.6441	-4.2327	-4.1536	-3.9514	-4.5400
sBAT	-3.9952	-3.7456	-4.3863	-4.2563	-4.0068	-4.6475
TCEP	-3.0087	-4.1681	-3.8788	-3.2117	-4.3711	-4.0818
OV-275	-2.6126	-3.8310	-3.4114	-2.7781	-3.9994	-3.5798
PAN	-3.6014	-3.6043	-3.7124	-3.8116	-3.8145	-3.9226
EAN	-3.6401	-3.7368	-3.7514	-3.8160	-3.9127	-3.9273

where $\Delta G_K^0(\text{CH}_2)$ = partial molar Gibbs free energy of solution for a methylene group

R = universal gas constant (1.987 cal/mole)

A = coefficient from Table II.

The partial molar Gibbs free energy of solution for the test probes was calculated using eqn. 8²¹. The data are summarized in Table V.

TABLE VI
PARTIAL MOLAR AND MOLAL GIBBS FREE ENERGY OF SOLUTION DIFFERENCE VALUES

Stationary phase	$\delta(\Delta G_K^0)_{SQ}^{PH}$			$\delta(\Delta G_M^0)_{SQ}^{PH}$		
	Ethanol	Nitromethane	Dioxane	Ethanol	Nitromethane	Dioxane
Squalane	0	0	0	0	0	0
OV-17	-0.437	-0.898	-0.324	-0.219	-0.680	-0.107
OV-105	-0.656	-0.552	-0.028	-0.528	-0.424	-0.100
OV-330	-1.267	-1.615	-0.479	-1.038	-1.386	-0.250
OV-225	-1.062	-1.539	-0.420	-0.847	-1.325	-0.206
QF-I	-0.489	-1.220	-0.161	-0.174	-0.905	-0.154
Carbowax 20M	-1.654	-2.150	-0.617	-1.425	-1.921	-0.401
DPAT	-2.235	-1.908	-0.729	-2.102	-1.775	-0.596
DEGS	-1.727	-1.993	-0.747	-1.406	-1.673	-0.426
BAT	-2.454	-1.692	-1.129	-2.333	-1.571	-1.008
sBAT	-2.603	-1.794	-1.283	-2.436	-1.627	-1.115
TCEP	-1.617	-2.216	-0.775	-1.391	-1.991	-0.550
OV-275	-1.221	-1.879	-0.308	-0.961	-1.619	-0.048
PAN	-2.210	-1.653	-0.609	-1.991	-1.434	-0.391
EAN	-2.248	-1.785	-0.648	-1.996	-1.533	-0.395

TABLE VII

SOLVENT SELECTIVITY PARAMETERS CALCULATED FROM DIFFERENCES IN PARTIAL MOLAR GIBBS FREE ENERGIES OF SOLUTION

Stationary phase	$\Sigma\delta(\Delta G)_{SQ}^{PHi}$	X_e	X_n	X_d
OV-17	-1.659	0.26	0.54	0.20
OV-105	-1.236	0.53	0.45	0.02
OV-330	-3.361	0.38	0.47	0.15
OV-225	-3.021	0.34	0.50	0.16
QF-1	-1.870	0.26	0.64	0.10
Carbowax 20M	-4.421	0.37	0.49	0.14
DPAT	-4.872	0.46	0.39	0.15
DEGS	-4.467	0.39	0.44	0.17
BAT	-5.275	0.47	0.32	0.21
sBAT	-5.680	0.46	0.32	0.23
TCEP	-4.608	0.35	0.48	0.17
OV-275	-3.408	0.36	0.55	0.09
PAN	-4.472	0.50	0.37	0.13
EAN	-4.681	0.48	0.38	0.14

$$\Delta G_K^0(P) = -2.303RT_c \log K_L^P \quad (8)$$

where $\Delta G_K^0(P)$ = partial molar Gibbs free energy of solution for solute P.

To assess the importance of molecular weight differences on the solvent selectivity parameters the molal Gibbs free energy of solution was used in some calculations (eqn. 9²¹). The data are summarized in Table V.

$$\Delta G_M^0(P) = -2.303RT_c \log \left(\frac{10^3 K_L^P}{RT_c \rho_c} \right) \quad (9)$$

where $\Delta G_M^0(P)$ = partial molal Gibbs free energy of solution
 ρ_c = liquid density at T_c .

The stationary phase densities and gas-liquid partition coefficients for butanol and nitropropane were taken from ref. 8. Solvent selectivity parameters were redefined in thermodynamic terms using eqns. 10 and 11. The letters e, n and d refer to ethanol, nitromethane and dioxane, respectively. The $\delta(G_K^0)_{SQ}^{PHi}$ and $\delta(G_M^0)_{SQ}^{PHi}$ values are summarized in Table VI and the solvent selectivity parameters in Table VII.

$$\delta(G_K^0)_{SQ}^{PHi} = (\Delta G_K^0i)^{PH} - (\Delta G_K^0i)^{SQ} \quad (10)$$

where $(\Delta G_K^0i)^{PH}$ = partial molar Gibbs free energy of solution of probe i
on phase PH

$(\Delta G_K^0i)^{SQ}$ = partial molar Gibbs free energy of solution of probe i
on squalane

$$x_i = \frac{\delta(\Delta G_K^0)_{SQ}^{PHi}}{\Sigma\delta(\Delta G_K^0)_{SQ}^{PHi}} \quad (11)$$

where $\Sigma\delta(\Delta G_K^0)_{SQ}^{PHi} = \delta(\Delta G_K^0)_{SQ}^{PHe} + \delta(\Delta G_K^0)_{SQ}^{PHn} + \delta(\Delta G_K^0)_{SQ}^{PHd}$.

RESULTS AND DISCUSSION

The calculation of solvent strength and solvent selectivity parameters according to Snyder for gas chromatographic solvents is based on the differences in retention index values for the test solutes ethanol, nitromethane and dioxane on two phases, one of which is the non-polar reference phase squalane. The retention value of the test solute on squalane is used as an approximate measure of dispersive interactions. Inductive interactions are ignored. This may be reasonable for test solutes with small dipole moments or at high temperatures where all orientations of the dipoles become equally probable. For nitromethane it could be reasonably argued that inductive interactions with squalane may be significant. Meyer *et al.*²² indicated that inductive interactions between dipolar solutes and *n*-tetracosane are on the order of 1 kcal/mol. However, the calculation method used by these authors to estimate the dispersive contribution to the total interaction energy is not well founded and may lead to an overestimation of the inductive energy contribution. Appropriate models are not available for the unequivocal determination of inductive energies. We draw the readers attention to this general problem in solution interactions but are unable to propose a solution at this time. The influence of an imperfect correction term on the use of the solvent selectivity triangle is unlikely to be great. The value of the test solutes on squalane acts as a scaling term which affects the absolute but not the relative accuracy of the solvent selectivity parameters. In other cases the inductive effect is combined with the orientation interaction and is hopefully weak for ethanol and dioxane whose retention is principally influenced by hydrogen bonding interactions.

In developing the theoretical model for the solvent selectivity triangle approach to stationary phase characterization it is assumed that the test solutes and *n*-alkanes used to establish the fixed points on the retention index scale are retained solely by gas-liquid partitioning. Adsorption of either the test solutes or *n*-alkanes at the support or liquid phase interfaces will lead to incorrect values for the retention index. The concurrent retention of solutes of strikingly different polarity to the liquid phase used for their separation by a mixed retention mechanism is a well established phenomenon (see, for example, refs. 7-9, 17 and 18), but one that has generally been ignored in methods used to characterize the solvent properties of liquid phases. Initial studies were directed towards establishing the contribution of interfacial adsorption to the solvent selectivity parameters for fifteen liquid phases spanning a wide polarity range.

Influence of interfacial adsorption on solvent selectivity parameters

The model used to estimate the contribution of interfacial adsorption to retention is based on the constancy of the observed partition coefficient at high phase loadings when the coefficient *B* in eqn. 2 can be considered zero. When *B* has a finite value the observed partition coefficient is no longer constant and varies with phase loading causing a slope or curvature in the observed data. Extrapolation to infinite liquid volume enables a value for the gas-liquid partition coefficient to be determined that is independent of the contribution from interfacial adsorption. For the liquid phases studied here three different categories of general behavior can be discerned. For those phases of low and moderate solvent strength (for example, squalane, OV-17, OV-105, OV-330, OV-225, QF-1 and Carbowax 20M), reasonable agreement with

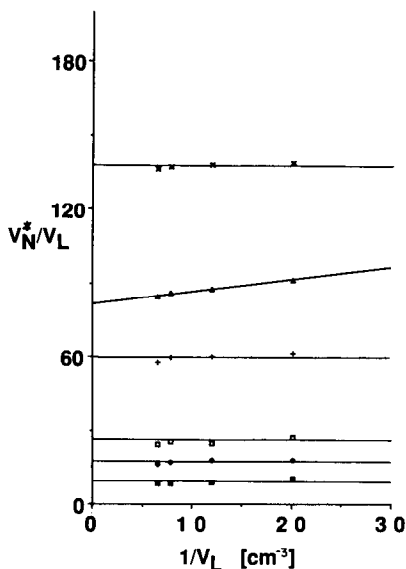


Fig. 1. Plot of V_N^*/V_L vs. $1/V_L$ for *n*-alkanes, ethanol, nitromethane and dioxane on squalane. Solutes: ■ = ethanol; ▲ = dioxane; ◆ = nitromethane; □ = pentane; + = hexane; × = heptane.

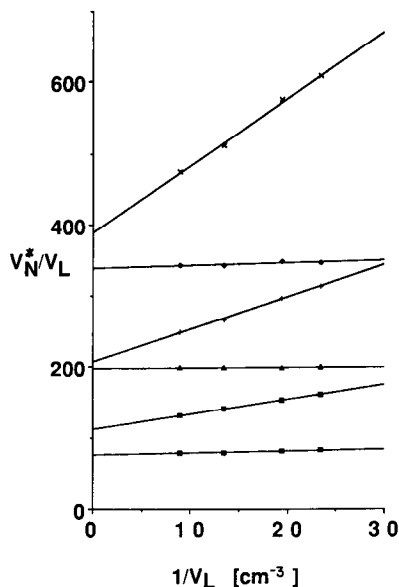


Fig. 2. Plot of V_N^*/V_L vs. $1/V_L$ for *n*-alkanes, ethanol, nitromethane and dioxane on Carbowax 20M. Solutes as in Fig. 1 except: □ = decane; + = undecane; × = dodecane.

a partition only model is found. By way of example the graphical data for squalane and Carbowax 20M are shown in Figs. 1 and 2. The difference between the measured retention index and the retention index value corrected for interfacial adsorption is generally small as indicated by the results in Table III. A second group of phases represented by the three thiocyanate salts show different behaviour to the first group. Using sBAT as a representative example (Fig. 3), both the test solutes and *n*-alkanes show substantial interfacial adsorption; the *n*-alkanes more so than the test probes. Linear extrapolation to infinite phase volume provides an accurate value for the gas-liquid partition coefficient. Large differences are now seen between the measured and corrected retention index values in Table III. Ignoring the contribution of interfacial adsorption to retention for these phases results in the calculation of misleading solvent selectivity parameters.

The remaining phases are perhaps among the most important from a classification point of view since they are the most polar of the phases evaluated. Taking DEGS and OV-275 (Figs. 4 and 5), as representative examples of the group which includes DEGS, TCEP, OV-275, PAN and EAN it can be seen that retention of the *n*-alkanes occurs almost entirely by interfacial adsorption. The polar test solutes are retained by a mixed retention mechanism and the gas-liquid partition coefficients can be obtained by linear extrapolation as for the other phases. Since, however, the *n*-alkanes do not partition significantly with these phases, meaningful retention index values can not be obtained. Consequently, it is not possible to calculate solvent selectivity parameters for these phases.

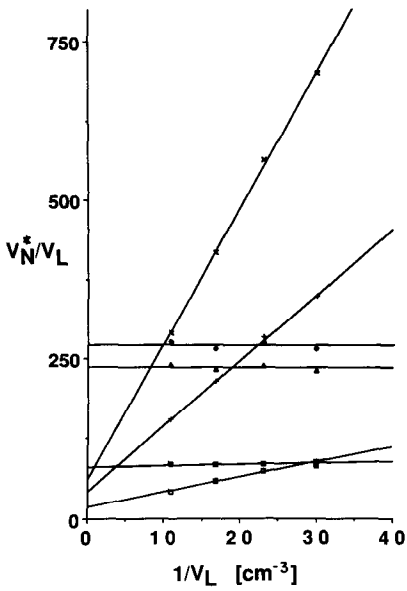


Fig. 3. Plot of V_N^*/V_L vs. $1/V_L$ for *n*-alkanes, ethanol, nitromethane and dioxane on *sec.*-butylammonium thiocyanate. Solutes as in Fig. 1 except: □ = pentadecane; × = hexadecane.

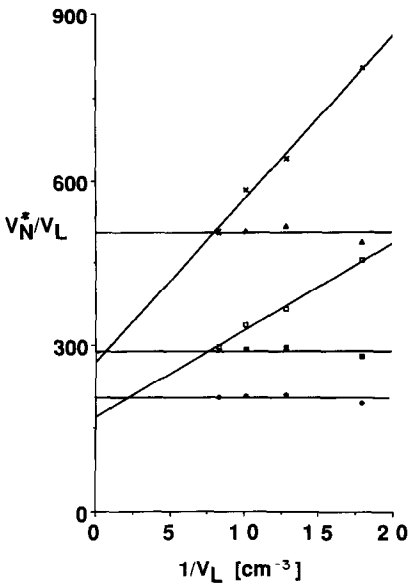


Fig. 4. Plot of V_N^*/V_L vs. $1/V_L$ for *n*-alkanes, ethanol, nitromethane and dioxane on poly(diethyleneglycol succinate). Solutes as in Fig. 1 except: □ = decane; × = dodecane.

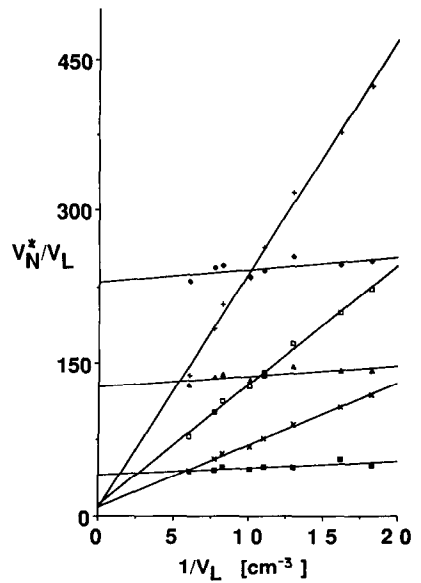


Fig. 5. Plot of V_N^*/V_L vs. $1/V_L$ for *n*-alkanes, ethanol, nitromethane and dioxane on OV-275. Solutes as in Fig. 1 except: × = dodecane; □ = tridecane; + = tetradecane.

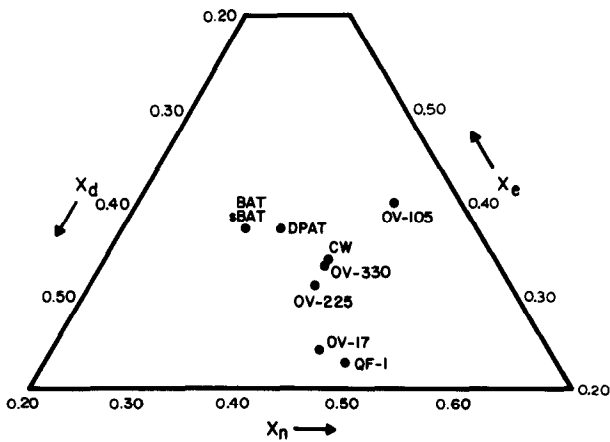


Fig. 6. Solvent selectivity triangle calculated using corrected retention indices.

The solvent selectivity parameters corrected for interfacial adsorption (Table IV), are plotted with triangular coordinates in Fig. 6. The phases evaluated can be grouped into four selectivity groups with Carbowax 20M, OV-330 and OV-225 forming one group, OV-17 and QF-1 a second, BAT, sBAT, and DPAT a third, and finally OV-105. A phase exhibiting minimum selectivity would be located at the center of the triangle. The most selective phases are found towards the corners of the triangle. None of the phases evaluated in Fig. 6 are highly selective as their location is centrally weighted compared to the selectivity space available. More selective phases, however,

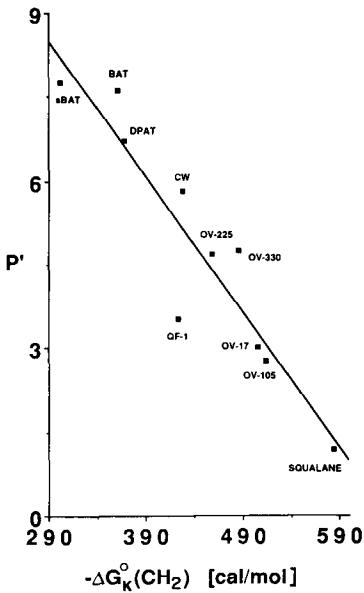


Fig. 7. Plot of $\Delta G_K^0(\text{CH}_2)$ against P' for phases that partition with n -alkanes.

could not be evaluated due to a failure of the calculation method caused by a lack of partitioning of the *n*-alkanes. A solution to this problem will be discussed subsequently.

Solvent polarity parameter

The solvent strength of a stationary phase can not be precisely defined since it is not a unique property of a solvent but a composite expression for several different interactions. Consequently, there is no single probe that can be defined as polar. The solvent polarity parameter equates polarity with the sum of the retention index increments for ethanol, nitromethane and dioxane corrected for the contribution from dispersion as indicated by eqn. 5. The approach proposed by Golovnya equates solvent strength with the reluctance of a stationary phase to retain a hydrocarbon. Quantitatively, this corresponds to the partial molar Gibbs free energy of solution for a methylene group (eqn. 7). In general, the agreement between the two scales is quite good (Table IV and Fig. 7) for those phases where a direct comparison is possible. A lack of partitioning of the hydrocarbons with some of the more polar phases evaluated (DEGS, TCEP, OV-275, PAN, EAN) excludes calculation of the solvent polarity parameter in those cases. For the remaining phases the solvent polarity parameter, P' , and the partial molar Gibbs free energy of solution for a methylene group, $\Delta G_K^0(\text{CH}_2)$, are related by eqn. 12

$$P' = 15.4559 + 0.0239[\Delta G_K^0(\text{CH}_2)] \quad n = 10 \quad r^2 = 0.859 \quad (12)$$

From Fig. 7 it is obvious that the data for QF-1 and OV-330 are more discordant than other members of the data set. Although the reason for this is not obvious if these two phases are removed a better correlation represented by eqn. 13 is obtained.

$$P' = 16.1149 + 0.0251[\Delta G_K^0(\text{CH}_2)] \quad n = 8 \quad r^2 = 0.966 \quad (13)$$

Eqn. 13 allows an estimate of P' values for liquid phases that partition with the 2-alkanones but not the *n*-alkanes. The estimated values are given in parentheses in Table IV. For those phases where a comparison is possible the $\Delta G_K^0(\text{CH}_2)$ values for the *n*-alkanes and 2-alkanones show good agreement.

An alternative estimation of the solvent polarity parameter is given by $\Sigma\delta(\Delta G_K^0)_{\text{SQ}}^{\text{PH}i}$ in eqn. 11. This represents the sum of the differences in the partial molar Gibbs free energy of solution of the test solutes ethanol, nitromethane, and dioxane on the polar phase and squalane as a non-polar reference phase. A good correlation exists between the free energy scale and the P' scale (Fig. 8) if the values estimated for DEGS, TCEP, OV-275, PAN and EAN are eliminated (eqn. 14).

$$P' = 0.4606 - 0.7908[\Sigma\delta(\Delta G_K^0)_{\text{SQ}}^{\text{PH}i}] \quad n = 9 \quad r^2 = 0.973 \quad (14)$$

The $\Delta G_K^0(\text{CH}_2)$ values used to estimate the P' values for the polar phases measures a quite general interaction whereas the $\Sigma\delta(\Delta G_K^0)_{\text{SQ}}^{\text{PH}i}$ scale sums only the three interactions measured by the test solutes. For the most polar phases these interactions are dominant and probably not adequately expressed by $\Delta G_K^0(\text{CH}_2)$.

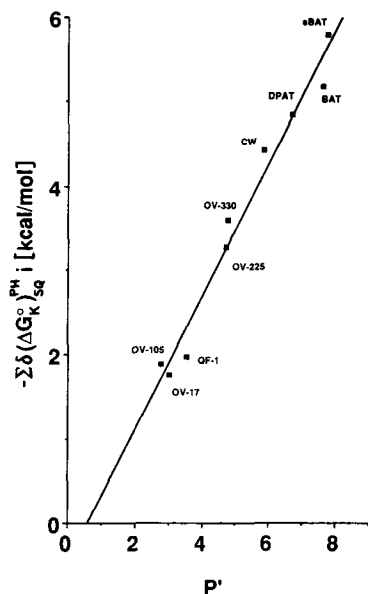


Fig. 8. Plot of $\Sigma\delta(\Delta G_K^0)^{PH}_i$ against P' for phases that partition with n -alkanes.

Solvent selectivity parameters measured on the free energy scale

Since the test solutes partition on all phases and solvent selectivity parameters cannot be obtained on polar phases due to a lack of partitioning of the n -alkanes it should be possible to derive a universally applicable selectivity scale based on the partition coefficients of the test solutes. These can be corrected for dispersion by subtraction of the solute partition coefficient for the test solutes on squalane and the results expressed as differences in the partial molar Gibbs free energy of solution. Since the phases to be evaluated span a wide molecular weight range both molar and molal Gibbs free energy differences were calculated (Table VI). The two scales are correlated well as indicated in eqns. 15–17.

$$\delta(\Delta G_K^0)^{PH}_{SQ} = 0.9628[\delta(\Delta G_M^0)^{PH}_{SQ}] - 0.2677 \quad \text{ethanol } n = 14 \quad r^2 = 0.994 \quad (15)$$

$$\delta(\Delta G_K^0)^{PH}_{SQ} = 1.0044[\delta(\Delta G_M^0)^{PH}_{SQ}] - 0.2100 \quad \text{nitromethane } n = 14 \quad r^2 = 0.975 \quad (16)$$

$$\delta(\Delta G_K^0)^{PH}_{SQ} = 0.9211[\delta(\Delta G_M^0)^{PH}_{SQ}] - 0.2478 \quad \text{dioxane } n = 14 \quad r^2 = 0.972 \quad (17)$$

Thus, ignoring differences in the molecular weights of the liquid phases will not seriously effect the accuracy of the solvent selectivity parameters.

The solvent selectivity parameters were calculated from the partial molar Gibbs free energy of solution for the test solutes using eqn. 11 and are summarized in Table VII. The data are shown diagrammatically in Fig. 9. Where a comparison is possible with Fig. 6 the grouping of the phases is not very different. What is more striking is that all phases are displaced substantially to the right in Fig. 9. This is due to a diminished contribution from proton-donor forces to retention on the scale derived from free energy differences. Analysis of the two sets of solvent selectivity parameters (Tables IV

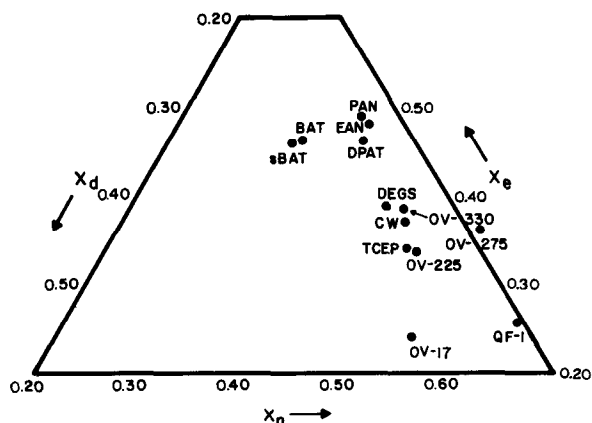


Fig. 9. Solvent selectivity triangle calculated using $\delta(\Delta G_k^0)_{SQ}^{PHi}$ values.

and VII) indicates that for OV-17, OV-225, QF-1, OV-330 and OV-105 the decrease in magnitude of X_d is largely compensated for by an increase in the X_n value while for DPAT, BAT and sBAT the decrease in X_d is largely compensated for by an increase in X_e . This would tend to indicate that either none of the phases evaluated have strong proton-donor properties or, alternatively, dioxane is a rather insensitive probe for proton-donor interactions.

The case for the selection of different test solutes

Snyder¹ selected ethanol, nitromethane and dioxane for his solvent selectivity scheme based on the availability of published data for over seventy solvents gathered by Rohrschneider²³; Rohrschneider used headspace analysis to measure the gas-liquid partition coefficients as most of the solvents evaluated were volatile liquids unsuitable as stationary phases for gas chromatography. One deficiency in the recommended test solutes for gas chromatography is their low retention on some phases even at moderate temperatures. The desire to measure solute-solvent interactions with an acceptable degree of accuracy presupposes sufficient residence time of the solute in the liquid phase to express this interaction with the desired experimental accuracy. Chromatographically the extent of liquid phase interactions as a function of the residence time of a solute in a column is indicated by the capacity factor. A selection of capacity factor values for the test solutes and some homologues or analogues recommended by McReynolds²⁴ for stationary phase characterization are given in Table VIII. As is readily apparent, the retention of ethanol and nitromethane on the non-polar phases is inadequate. This will, of course, influence the accuracy with which the retention of the test solutes on squalane can be taken as an approximate measure of dispersive interactions. If it is accepted that a capacity factor of at least 5 is desirable and a value greater than 20 is preferred, then ethanol and nitromethane are inadequate as test solutes. Dioxane is marginally acceptable. New probes should be selected for the accurate determination of solvent selectivity parameters for gas chromatographic purposes.

Gas-liquid partition coefficients for *n*-butanol, nitropropane, 2-pentanone and pyridine at 80.8°C have been determined for many of the phases used in this study⁶.

TABLE VIII

CAPACITY FACTOR VALUES FOR TEST SOLUTES ON DIFFERENT STATIONARY PHASES (PHASE LOADING 12–15%, w/w) AT 80.8°C

Stationary phase	Capacity factor					
	Ethanol	Nitromethane	Dioxane	Butanol	Nitropropane	Pyridine
Squalane	0.46	0.89	4.65	2.81	4.6	6.56
OV-17	0.41	1.76	4.00	2.14	6.1	5.97
OV-105	0.84	1.47	3.39	3.60	5.07	4.71
OV-330	1.41	5.05	5.14	6.35	11.19	9.24
OV-225	1.35	5.97	6.26	5.65	15.97	10.56
QF-1	0.39	2.55	2.76	1.52	7.64	4.03
Carbowax 20M	3.26	14.24	8.26	12.21	20.03	16.97
DPAT	7.00	9.24	9.30	23.39	18.91	
DEGS	2.16	7.03	6.09	6.22	9.59	
BAT	8.33	6.30	14.33	24.33	11.12	
sBAT	11.03	7.67	18.89	29.81	13.42	
TCEP	2.24	11.97	7.88	6.52	17.30	13.61
OV-275	1.39	6.82	3.82	3.61	9.52	7.33
PAN	4.68	4.70	5.42	10.69	5.33	
EAN	4.52	6.80	6.93	10.31	5.81	

These probes are better retained on most phases (Table VIII), but are not necessarily ideal. Pyridine, in particular, is of questionable value as its peak shape on several phases is asymmetric resulting in inaccurate partition coefficients. These additional probes can be used to determine whether the choice of the test solute influences the position of a particular phase in the solvent selectivity triangle.

There is a reasonable correlation between the partial molar or molal Gibbs free energy and energy differences $\delta(\Delta G)$ for ethanol and butanol.

$$\delta(\Delta G_{\text{K}}^0)_{\text{butanol}} = 0.7705[\delta(\Delta G_{\text{K}}^0)_{\text{ethanol}}] + 0.1338 \quad n = 14 \quad r^2 = 0.924 \quad (18)$$

$$\delta(\Delta G_{\text{M}}^0)_{\text{butanol}} = 0.7301[\delta(\Delta G_{\text{M}}^0)_{\text{ethanol}}] + 0.1030 \quad n = 14 \quad r^2 = 0.913 \quad (19)$$

Scrutiny of the data indicates two separate trends for phases that can be separated by their ability to partition with the *n*-alkanes. This is most apparent in the data for $\delta(\Delta G_{\text{M}}^0)$ where the polar phases DEGS, OV-275, TCEP, EAN and PAN are displaced to the right of the other phases and form a second quasi linear relationship (Fig. 10). The fluorine-containing phase QF-1 is perhaps a little ambiguous or exceptional as it fits better with the data for the polar phases rather than with those phases having similar solvent strength. If the polar phases are removed from the correlation the agreement between the two test solutes improves ($r^2 = 0.985$, $n = 9$) for both the molar and molal scale. Changing ethanol for butanol will have a small effect on the selectivity parameters of the moderately polar phases but will produce a systematic change for the polar phases.

There is no correlation between either the Gibbs free energies or the differences in free energy after subtraction of the value on squalane for the test solutes

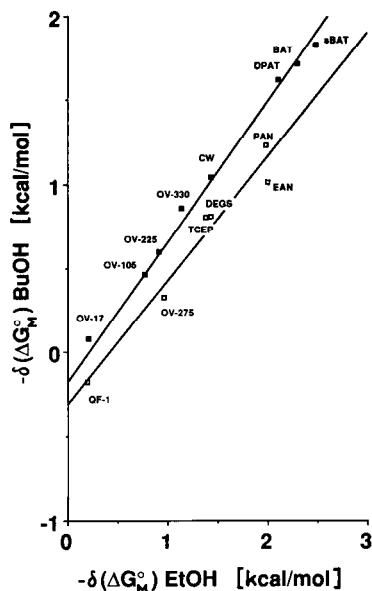


Fig. 10. Plot of $\delta(\Delta G_M^0)_{\text{BuOH}}$ against $\delta(\Delta G_M^0)_{\text{EtOH}}$.

nitromethane and 1-nitropropane. This is not surprising since the retention of the first member of a homologous series is frequently anomalous compared to expectations predicted from higher members of the series. On some phases it was noted that nitromethane eluted after 1-nitroethane. Thus, nitromethane does not behave characteristically of the other nitroalkanes on most selective phases. The use of higher-molecular-weight nitroalkanes in place of nitromethane will significantly change the relative position of a phase in the selectivity triangle in an unpredictable manner.

2-Pentanone and pyridine were evaluated as alternative test solutes for dioxane. Again there was no correlation between the free energies or their differences after subtraction of the value for the test solutes on squalane. The value of the solvent selectivity parameter will consequently be influenced by the choice of test solute. Part of the reason in this case may be that both pyridine and 2-pentanone have reasonably large dipole moments (≈ 2.5 D) compared to dioxane (≈ 0.45 D) and consequently their retention will be more influenced by orientation interactions than is the case for dioxane.

CONCLUSIONS

The solvent selectivity parameter approach is a useful tool for characterizing the solvent properties of liquid phases. The method as proposed by Snyder has certain limitations when applied to gas chromatographic solvents. A lack of partitioning of the *n*-alkanes with polar phases precludes the calculation of selectivity parameters for these phases. Inadequate retention of the test solutes on many phases, particularly those of low polarity, adversely influences the accuracy with which selectivity parameters can be measured. The position of a phase within the selectivity triangle is

a function of the test solutes used and will vary even for homologues of the test solutes suggested by Snyder.

To make the solvent selectivity parameters more useful for classifying liquid phases it will be necessary to select a new group of test solutes with sufficient retention to enable accurate measurements on phases spanning a wide range of solvent strength. To discontinue the use of the retention index scale for the measurement of retention in favor of using the gas-liquid partition coefficient of each test solute or some function, such as the Gibbs free energy of solution, easily derived from it. To evaluate further the contribution made by dispersion to the solvent selectivity parameters and define suitable methods of allowing for its effect. With these changes the solvent selectivity triangle approach to stationary phase characterization can be made more universally useful.

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